SYNTHETIC AND STRUCTURAL STUDIES OF MONOTHIOACID COMPLEXES OF RUTHENIUM

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Ph.D. Thesis

University of Edinburgh

1978

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DECLARATION

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole or in part, for any other degree. Certain of the results presented have already been published.

In memory of my parents

ACKNOWLEDGMENTS

My thanks are due to many people who have helped in the planning and execution of the work presented in this thesis.

My supervisors, Dr. R.O. Gould and Dr. T.A. Stephenson, have been generous with their time and their enthusiasm throughout the project.

Dr. R. Nelmes of the Physics Department at Edinburgh University, Dr. J.H. Noordik of the Chemistry Department at the Catholic University in Nijmegen and Dr. P. Murray-Rust of the Chemistry Department at Stirling University all kindly allowed me to collect X-ray data on the automatic diffractometers in their respective departments.

Dr. A.S.F. Boyd and Mr. J. Millar ran ^{31}P- and ^{1}H-n.m.r. spectra and all my colleagues in the department, particularly Mr. J.A. Goodfellow, have been extremely helpful.

Mrs. R.W. Chester was responsible for typing the thesis, under considerable pressure of time, and I am most grateful to her.

ABSTRACT

Chapter 1 reviews the known monothioacid compounds of transition metals and some d^0 and d^{10} metals.

Chapter 2 deals with the reactions of mer-$RuCl_3(PMe_2Ph)_3$ and $RuCl_2(PPh_3)_3$ with sodium and ammonium monothiobenzoate to give $Ru(PhCOS)_2(PR_3)_2$ compounds. The reactions of the products with some monodentate Lewis bases are discussed together with the X-ray structure analysis of the unexpected product $Ru(PhCOS)_2(PMePh)_2(HNCMeCH_2CMe_2NH_2)$.

Chapter 3 describes the reactions of $Ru(PhCOS)_2(PMe_2Ph)_2$ with bidentate nitrogen-donor Lewis bases, L_2 (L_2 = en, bipy or phen) to give $Ru(PhCOS)_2(PMe_2Ph)_2(phen)$ compounds, and the X-ray structure analysis of two isomers of $Ru(PhCOS)_2(PMe_2Ph)_2(phen)$.

Chapter 4 describes the reactions of $Ru(PhCOS)_2(PMe_2Ph)_2$ with bidentate phosphorus-donor Lewis bases, Q_2 (Q_2 = mediphos or etdiphos), and the X-ray structure analysis of $Ru(PhCOS)_2(PMe_2Ph)(etdiphos)$.

Chapter 5 deals with the reactions of $RuCl_2(PR_3)_{3 \text{ or } 4}$ compounds (PR_3 = PMe_2Ph, $PMePh_2$, $P(OMe)_2Ph$ or $P(OMe)Ph_2$) with monothiobenzoate ion to give $Ru(PhCOS)_2(PR_3)_{2 \text{ or } 3}$ compounds. The isolation of intermediates in the formation of mer-$Ru(PhCOS)_2(PMe_2Ph)_3$, namely $[Ru(PhCOS)(PMe_2Ph)_4][BPh_4]$ and fac-$Ru(PhCOS)_2(PMe_2Ph)_3$, is discussed.

Appendix 1 describes X-ray structure determinations carried out on $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$ and $[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$, and discusses the formation of these anions from $[RuCl_2(CO)(C_7H_8)]_2$.

C O N T E N T S

C O N T E N T S (Contd.)

C O N T E N T S (Contd.)

C O N T E N T S (Contd.)

FIGURES

TABLES

TABLES

SCHEMES

CHAPTER 1

MONOTHIOACID COMPLEXES OF TRANSITION METALS AND SOME OTHER METALS

Over the last fifteen years, a good deal of work has been published on metal complexes containing dioxo[1]- and dithioacid[2] ligands. More recently, some attention has been given to the use of monothioacids as ligands. A monothioacid may be regarded as being derived from the corresponding dioxoacid by substituting a sulphur atom for one of the functional oxygen atoms. This increases the number of different modes of coordination available when the acid acts as a ligand, and widens the scope for isomerism in its compounds. The different donor and acceptor properties of oxygen and sulphur, illustrated in the coordination chemistry of the dioxo- and dithioacids, will also be important in determining the behaviour of monothioacid ligands in metal complexes.

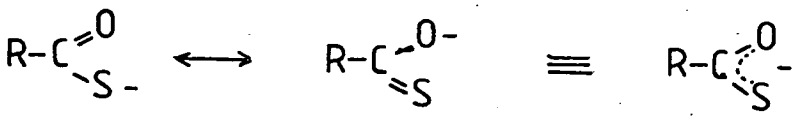
Most of the work which will be presented in the later chapters deals with the behaviour of the monothiobenzoate ion in ruthenium(II) complexes, and the results so far published on monothiocarboxylate complexes will be reviewed in detail, together with a briefer account of the behaviour of other monothioacid ligands. Four types of monothioacid have been studied as coordinating ligands in transition metal complexes:

	(i)	monothiocarboxylates	$RCOS^-$
	(ii)	monothioxanthates	$ROCOS^-$
	(iii)	monothiocarbamates	R_2NCOS^-
and	(iv)	monothiophosphinates	R_2POS^-

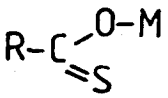
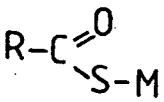
Each type of ligand will be dealt with separately, since varying amounts of data are available on each type.

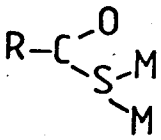
(i) Monothiocarboxylates $RCOS^-$

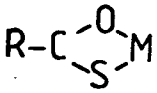
The structure of a monothiocarboxylate ion can be represented as a resonance hybrid of two canonical forms:

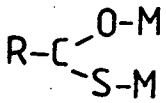


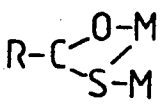
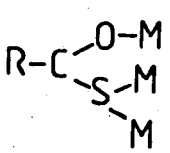
In a metal complex, a number of different modes of coordination are possible:

A unidentate  or 

B unidentate (bridging through S) 

C bidentate (chelated) 

D bidentate (bridging) 

E bidentate (doubly bonded S)  or 

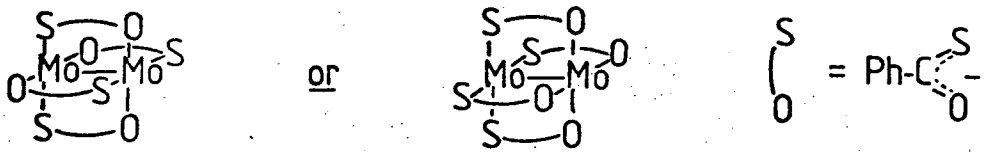
Neither of the bidentate modes with a doubly bonded sulphur atom has been reported, although they are fairly common among monothiocarbamates and monothiophosphinates, but all the other modes of coordination have been characterised.

(a) Binary Compounds

Monothiobenzoate and monothioacetate are the two most studied monothiocarboxylate ligands, and binary compounds of monothiobenzoate are known for Cr(III)[3,4], Mo(II)[5], Co(II)[6], Ni(II)[4,7,8,9,10], Pd(II)[11,12], Pt(II)[12], Cu(I)[4], Ag(I)[4], Zn(II)[4], Cd(II)[4], Hg(II)[4] and Pb[8]. A similar monothioacetate is known for Ni(II)[10] only, and the analogous Ni(II) monothiopropionate has also been reported[10]. In general, the benzoates were prepared by adding sodium monothiobenzoate to an aqueous solution containing the appropriate metal ion, although the Ni(II) complex was prepared in ethanol, and the Pd(II) and Pt(II) complexes from $PdCl_2$[11] or $\left[Pd(MeCO_2)_2\right]_3$[12] and Na_2PtCl_4[11] respectively. In characterising the monothiobenzoate complexes, Savant, Gopalakrishnan and Patel[4] analysed the characteristic stretching modes in the i.r. spectra of the compounds. They found that $\nu_{(CO)}$ and $\nu_{(CS)}$ are both sensitive to the mode of coordination and they assigned structures to a series of metal monothiobenzoates by comparing these frequencies with those in the spectrum of the completely ionic sodium salt. For the sodium salt, $\nu_{(CO)}$ is observed at 1500 cm^{-1} and $\nu_{(CS)}$ at 960 cm^{-1}. Each of the five expected bonding modes shows characteristic shifts in $\nu_{(CO)}$ and $\nu_{(CS)}$ viz. the bidentate modes (C and D on page 2) show little change, or a slight lowering in frequency of both $\nu_{(CO)}$ and $\nu_{(CS)}$. In practice, distinctions between bridging and chelated monothiobenzoate groups made on the basis of i.r. evidence are not reliable. The two unidentate modes bonded through sulphur (A and B) show a raising of $\nu_{(CO)}$ and a lowering of $\nu_{(CS)}$

relative to the values for sodium monothiobenzoate, due to the increased double-bond nature of the C-O bond and the increased single-bond, or mercaptide, nature of the C-S bond. In the case of unidentate bonding through oxygen, the same kind of reasoning leads to a lowering of $\nu_{(CO)}$ and a raising of $\nu_{(CS)}$. On this basis, structures have been proposed for several of the metal monothiobenzoates by Savant et al.[4]. Of those discussed, only $[Cr(PhCOS)_3]$ was shown to be monomeric in solution; $\nu_{(CO)}$ at 1465 cm^{-1} and $\nu_{(CS)}$ at 982 cm^{-1} indicate that coordination is stronger through the oxygen atom, although it seems unlikely that the sulphur is completely uncoordinated, as the magnetic moment of 3.72 indicates octahedral coordination about the Cr(III).

The Mo(II) species $[Mo(PhCOS)_2]_2$, made by reacting Mo(II) acetate with ammonium monothiobenzoate[5], has been shown to be dimeric from analysis of its mass spectrum, and in the i.r. spectrum $\nu_{(CO)}$ at 1465 cm^{-1} and $\nu_{(CS)}$ at 960 cm^{-1} are consistent with a bidentate bridging structure (1).



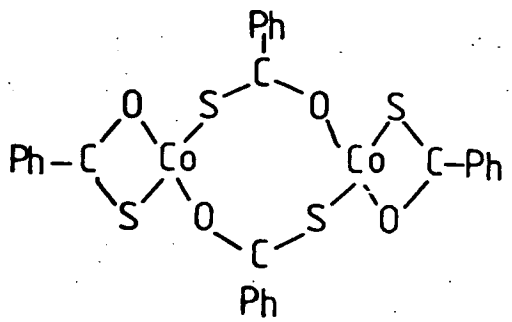
(1)

This is analogous to the structure of $[Ni_2(PhCOS)_4.EtOH]$ discussed later[9], and indeed to the molybdenum acetate structure itself.

In $[Cu(PhCOS)]$ and $[Ag(PhCOS)]^4$, $\nu_{(CO)}$ at 1570 cm^{-1} and 1612, 1583 cm^{-1} respectively and $\nu_{(CS)}$ at 935, 910 cm^{-1} and 924, 910 cm^{-1} indicate strong sulphur coordination with the oxygen possibly completely uncoordinated. On the basis of molecular weight measurements, oligomeric or polymeric units are clearly present in solution and further study is needed to determine whether these structures are, for instance, chains or clusters.

In $[Zn(PhCOS)_2]$ and $[Cd(PhCOS)_2]$, $\nu_{(CO)}$ is observed at 1545 cm^{-1} and 1590 cm^{-1} respectively and $\nu_{(CS)}$ at 955, 928 cm^{-1} and 930 cm^{-1}, indicating that while coordination is undoubtedly stronger through sulphur, the monothiobenzoate group is probably still bidentate. However, it is again clear that these complexes are not monomeric, and structures cannot be unambiguously assigned. In $[Hg(PhCOS)_2]$, $\nu_{(CO)}$ at 1630 cm^{-1} and $\nu_{(CS)}$ at 912 cm^{-1} suggest that coordination is entirely through sulphur, and a polymeric structure of mercury atoms bridged by sulphurs is proposed, but cannot be confirmed on i.r. data alone.

The monothiobenzoate complex of Co(II) shows a number of interesting features[11]. The complex is formulated as a dimer, $[Co_2(PhCOS)_4]$, and electronic spectra indicate pseudo-tetrahedral coordination around each metal, suggesting structure (2), although other forms of bridging cannot be ruled out.

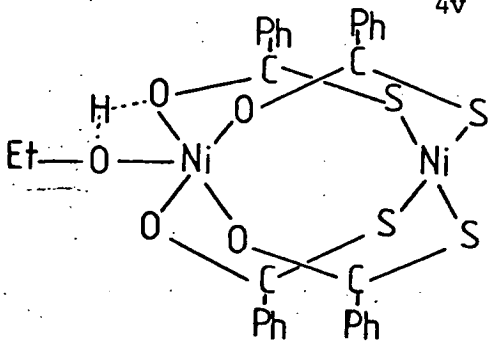


(2)

Magnetic susceptibility data show magnetic coupling of the two Co(II) centres. Here, the monothiobenzoate is behaving like some dioxocarboxylate ligands in its ability to promote magnetic coupling[14,15,16] and like some dioxo-, monothio- and dithiophosphinates in its mode of bridging[17]. Co(III) monothiobenzoate complexes proved unobtainable as reaction mixtures containing Co(III) yielded dibenzoyl disulphide, the oxidation product of monothiobenzoic acid, and Co(II) species. This contrasts with the behaviour of dithiocarboxylates which give only Co(III) octahedral complexes[13], and no Co(II) species.

The binary monothiobenzoate of Ni(II) has been reported by several workers[4,7,8,9,10]. Together with the monothioacetate and

monothiopropionate[10] complexes it is formulated as a dimer $[Ni_2(RCOS)_4.EtOH]$ with a structure (3) which has been confirmed by X-ray crystallography[9]. The structure determination revealed a molecule containing one nickel atom coordinated to four sulphurs, with local D_{4h} symmetry, and one nickel coordinated to five oxygens, with local C_{4v} symmetry.



(3)

The observed magnetic moment of the dimer, 2.40 per nickel, is attributed to two unpaired electrons on the NiO_5 unit, which is subject to a relatively weak ligand field, while the square-planar NiS_4 unit produces a strong ligand field and ensures spin-pairing at this end of the dimer[10]. Analogous bridged, dimeric structures are postulated for $[Ni_2(MeCOS)_4.EtOH]$ and $[Ni_2(EtCOS)_4.EtOH]$[10]. The i.r. spectra of the three complexes are consistent with this bridged coordination, with $\nu_{(CO)}$ at 1508 cm^{-1}, 1540 cm^{-1} and 1580 cm^{-1} for the $PhCOS^-$, $MeCOS^-$ and $EtCOS^-$ complexes respectively, compared with values of 1690-1700 cm^{-1} for the free acids, and $\nu_{(CS)}$ at 958 cm^{-1} for the $PhCOS^-$ complex, compared with 960 cm^{-1} in the sodium salt. However, these values would be equally consistent with symmetrical chelation of the ligands, as was proposed for "$Ni(PhCOS)_2$" by Savant et al.[4], and this illustrates the unreliability of i.r. spectra as a test for bridged versus chelated coordination. Hieber and Brück[7] reported that the solubility of "$Ni(PhCOS)_2$" in water was increased by adding excess monothiobenzoate ion, and they attributed this to the formation of $[Ni(PhCOS)_4]^{2-}$ ions in solution. However the species has not been isolated or further characterised.

Oro et al. reported in 1972[11] the preparation of $[Pd(PhCOS)_2]$ from $PdCl_2$ in aqueous solution. More recent workers[12] have used

$[Pd(MeCO_2)_2]_3$ as starting material and have similarly prepared $[Pt(PhCOS)_2]$ from Na_2PtCl_4. The molecular weight of the Pd(II) complex is concentration dependent, varying between 1100 (trimeric) and 1700, and the formulation $[Pd(PhCOS)_2]_n$, with $n \geq 3$, is suggested. The i.r. spectrum ($\nu_{(CO)} = 1675\ cm^{-1}$, $\nu_{(CS)} = 880\ cm^{-1}$) indicates that the polymer is sulphur-bridged, with the oxygen uncoordinated (cf. $[Hg(PhCOS)_2]$[4], discussed earlier.) $[Pt(PhCOS)_2]$ is too insoluble for molecular weight studies, and the i.r. spectrum ($\nu_{(CO)}$ at 1660, 1595 and 1575 cm^{-1} and $\nu_{(CS)}$ at 920 and 880 cm^{-1}) may indicate that more than one mode of monothiobenzoate bonding is present, although all modes clearly involve strong Pt - S and weak Pt - O coordination. The structure cannot be fully characterised, but it is probably made up of $[Pt(PhCOS)_2]_n$ oligomers or polymers.

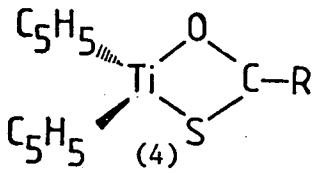
Finally, a lead complex of monothiobenzoic acid is used[8] as a plasticising agent for natural rubber. It is prepared in aqueous solution, but no structural details are available.

(b) Compounds Containing Other Ligands

Complexes which fall under this heading have been prepared by workers in two main areas: firstly, those who have examined the coordination properties of monothioacid ligands and the behaviour of monothioacid complexes in the presence of, principally, Lewis bases. Secondly, there are those who have used monothiocarboxylates as pseudo-halides in studying, for example, oxidative addition reactions.

Thus, a series of Ti(III) compounds with the general formula $[(\eta^5\text{-}C_5H_5)_2Ti(RCOS)]$ has been synthesised[18] where R = H, Me, Pr, $CH_3(CH_2)_{16}$ or Ph. These complexes were prepared in air-free aqueous solutions and are oxidised in air to give Ti(IV) products containing a Ti-O-Ti linkage, and free monothioacid. Molecular weight measurements indicate that the

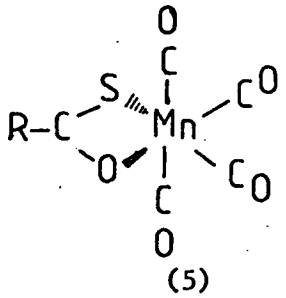
complexes are monomeric, and magnetic measurements show one unpaired electron per titanium. A band occurring in the i.r. spectra of all the complexes at 1390-1435 cm^{-1} is attributed to a stretching mode of the $-COS^-$ group described by Nyquist and Potts[19] as "analogous to the asymmetric stretch of carboxyl groups" and assigned to bands in the region 1520-1530 cm^{-1} in the free acids. The lowering of this frequency in the complexes, and conductivity evidence of covalent bonding, lead to the proposal of a general structure (4) for these complexes, analogous to the structure proposed for $[(\eta^5\text{-}C_5H_5)_2Ti(RCO_2)]$ species[20].



(4)

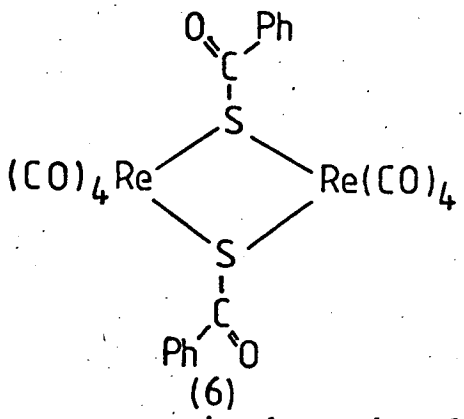
Since various cyclopentadienyl ring modes obscure the regions of the i.r. spectrum where $\nu_{(CO)}$ and $\nu_{(CS)}$ might be predicted according to Savant et al.[4], interpretation on that basis would be difficult.

Mn(I)[21] and Re(I)[22] complexes of monothiobenzoic and (in the case of Mn(I)) monothioacetic acid have been prepared from the appropriate metal carbonyl halides in THF solvent. For example, $Mn(CO)_5Br$ with RCOSH (R = Ph, Me) yields $[Mn(CO_4(RCOS)]$. In the i.r. spectra $\nu_{(CO)(acid)}$ is observed at 1660 cm^{-1} (R = Ph) and 1683 cm^{-1} (R = Me) as against 1690 cm^{-1} and 1712 cm^{-1} in the free acids, and it is argued that this suggests coordination through oxygen as well as sulphur, although values lower than this have been found in several cases where there is no oxygen coordination[4,10,12]. The four carbonyl stretching modes observed in each case can be interpreted as the 3A' + A" modes arising from a molecule of C_s symmetry and structure (5) is proposed for both species.



(5)

In contrast, $Re(CO)_5C\ell$ reacts with PhCOSH to give a product which is characterised as a dimer (6).

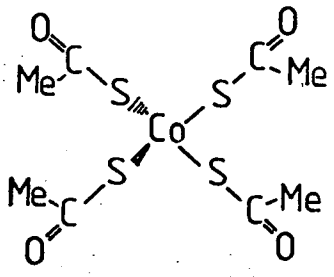


(6)

In the i.r. spectrum $\nu_{(CO)(acid)}$ is observed at 1685 cm^{-1}, very close to the value for the free acid, and $\nu_{(CS)}$ is at 880 cm^{-1}, much lower than in the sodium salt. This suggests that the monothiobenzoate is unidentate, bridging through the sulphur (cf. $[M(PhCOS)_2]$, M = Hg[4], Pd[12], discussed earlier). This type of complex is well known with mercaptide-sulphur bridges[23,24,25], suggesting high mercaptide character in the sulphur of the monothiobenzoate ion. However, $Re(CO)_5C\ell$ reacts with MeCOSH in THF to give a dimeric solvent adduct $[Re(CO_3(THF)C\ell]_2$. The acid adduct $[(MeCOSH)Re(CO)_3C\ell]$ is suggested as a possible intermediate, but no monothioacetate complex of rhenium has been characterised.

The monothioacetate ion has been used as a pseudo-halide in the substitution reactions of $[AsPh_4]_2[MC\ell_4]$[26] (M = Co(II) or Zn(II)) and in each case the $[M(MeCOS)_4]^{2-}$ ion was obtained. $[Co(MeCOS)_4]^{2-}$, which has been prepared previously[27] but was characterised as the double salt $(MeCOS)_2Co.2\ MeCOSNH_4$, gives an i.r. spectrum in which $\nu_{(CO)}$

is observed at 1615 cm^{-1} and ligand field splitting parameters calculated from electronic spectra are consistent with tetrahedrally coordinated Co(II). The structure (7) is proposed, with the monothioacetate unidentate through sulphur. The Zn(II) ion $[Zn(MeCOS)_4]^{2-}$

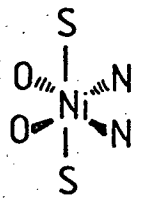


(7)

was also prepared and is assigned a tetrahedral structure by analogy with the tetrachlorozincate ion[28], presumably with monodentate sulphur-coordinated ligands. Attempts to synthesise the trifluoromonothioacetate analogues of these anions produced only Co(II) and Zn(II) sulphides, and the reaction of $[NiCl_4]^{2-}$ with MeCOSH resulted in a brown oil which could not be characterised (but see reference 6).

The reactions of Ni(II)[10,12,29], Pd(II)[11,12] and Pt(II)[12] monothiobenzoates and (in the case of Ni(II)) monothioacetate with a range of nitrogen and phosphorus Lewis bases, and the structures[30,31] of the products, have received a good deal of attention. $[Ni_2(PhCOS)_4.EtOH]$ has been reacted with a wide range of unidentate and bidentate nitrogen donors including py[29], α-, β- and γ-picoline[29], 4-picolinaldehyde[29], quinoline[29], bipy[12] and phen[12] to give a series of monomeric, paramagnetic, octahedral complexes of general formula $[Ni(PhCOS)_2L_2]$ where L = unidentate base or L_2 = bidentate base. The monothiobenzoate group is coordinated as a bidentate chelate in these complexes, and in the case of the unidentate base adducts, $[Ni(PhCOS)_2]_2$ can be recovered on heating[29]. The ligand field splitting parameter 10Dq increases on adduct formation, parallel to the electron-donor capacity of the base used[29]. A similar series of reactions of $[Ni_2(PhCOS)_4.EtOH]$ with phosphorus-donor Lewis

acids yields a series of adducts which are strikingly different. $[Ni(PhCOS)_2Q_2]$ where Q = PPh_3, $PMePh_2$, PMe_2Ph or Q_2 = mediphos, etdiphos have all been prepared and characterised[12]. These monomeric products are diamagnetic and are believed to be square-planar in coordination, with the monothiobenzoate acting as a unidentate ligand through sulphur. Presumably the more basic phosphine ligands, with their π-acceptor capacity, are more readily able to rupture the Ni-O bonds in the starting material and are high enough in the spectrochemical series to force the Ni(II) to adopt a low-spin square-planar configuration. Similar results have been obtained for $[Ni_2(MeCOS)_4.EtOH]$ and its Lewis base adducts[10,12]. An X-ray structure determination for $[Ni(MeCOS)_2(py)_2]$[30] confirms that it is monomeric and octahedral with bidentate, chelated monothioacetate groups. The environment of the nickel is as shown in figure (8), with <u>trans</u>-sulphurs, <u>cis</u>-oxygens and <u>cis</u>-nitrogens. Whether this is a general pattern



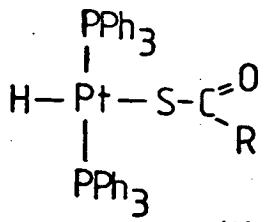
(8)

in the coordination of these nitrogen-base adducts remains to be seen, although clearly some arrangement with <u>cis</u>-nitrogens must occur in the bidentate base adducts.

The pyridine adduct of $[Pd(PhCOS)_2]_n$ has been known for some time[11] and is formulated as a monomer $[Pd(PhCOS)_2(py)_2]$. This work has recently been extended to include $[Pt(PhCOS)_2]_n$ and a wider range of bases, and a series of complexes $[M(PhCOS)_2L_2]$ has been produced, where M = Pd or Pt and L = py, PPh_3, $PMePh_2$, PMe_2Ph, $AsPh_3$ and $SbPh_3$. The complexes

are all monomeric and with no scope for octahedral geometry even pyridine gives square-planar coordination with the monothiobenzoate groups unidentate through sulphur (i.r. evidence). Hydrogen-1- and $^{31}P-\{^{1}H\}$-n.m.r. studies indicate that a trans geometry is preferred, and an X-ray crystal structure analysis of $[Pd(PhCOS)_2(PMe_2Ph)_2]$[31] confirms this, with the molecule lying on a crystallographic centre of symmetry.

The oxidative addition of PhCOSH and MeCOSH to the Pt(0) species $Pt(PPh_3)_4$ has been studied[32], and a stable product $[PtH(RCOS)(PPh_3)_2]$ was obtained with R = Ph or Me. In the i.r. spectra, $\nu_{(CO)}$ appears at 1595 cm^{-1} (R = Ph) and 1625 cm^{-1} (R = Me), consistent with unidentate coordination through sulphur and the structure (9) is proposed for both complexes. The $\nu_{(Pt-H)}$ vibration



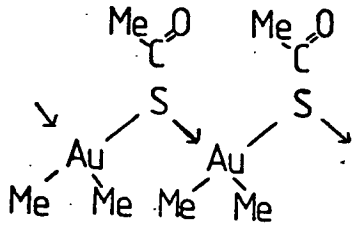
(9)

is found in the spectra of the two complexes at 2125 cm^{-1} and 2140 cm^{-1} respectively, values lower than expected for Pt(II) hydrides and this is attributed to the fairly high trans influence of the sulphur-donor ligands, which is also reflected in the ^{1}H-n.m.r. chemical shifts of the hydride protons.

One monothioacetate complex of Ru(II) has been briefly reported[33]. $[Ru(MeCOS)_2(PPh_3)_2]$ was obtained by reacting $[RuCl_2(PPh_3)_3]$ with sodium monothioacetate, but no structural or spectroscopic details are available. Presumably the complex is octahedral, with bidentate, chelated monothioacetate groups. Recently a monothioformate Ru(II) complex characterised as $[Ru(HCOS)(PMe_2Ph)_4][PF_6]$ has been reported[34]. It is formed by the insertion of COS into the Ru-H bond of $[RuH(PMe_2Ph)_5][PF_6]$, and the

coordination of the $HCOS^-$ ligand is presumably bidentate, chelated.

The only known gold complex of a monothiocarboxylate is $[Me_2Au(MeCOS)]$, prepared from $Me_3Au(OEt)_2$ and monothioacetic acid[35]. This is formulated as a sulphur-bridged polymer (10).

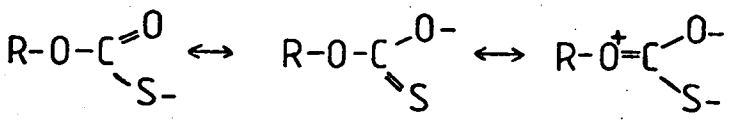


(10)

In the i.r. spectrum, $\nu_{(CO)}$ is observed at 1700, 1710 cm^{-1}, close to the value for the free acid, and bands at 1266 and 958 cm^{-1} are assigned as $\nu_{(CS)}$. The complex is very insoluble and explodes on heating.

(ii) O-alkyl Monothiocarbonates (monothioxanthates) $ROCOS^-$

Much less work has been published on monoathioxanthates than on the other classes of monothioacid, and much of that which has appeared has been concerned with the analysis of i.r. spectra of alkali-metal salts and simple binary complexes. The monothioxanthate ion can be represented as a hybrid of three canonical forms:



Normal coordinate analysis of the i.r. spectra of alkali metal salts of $MeOCOS^-$ [36,37] and $EtOCOS^-$ [37] indicates that in the uncoordinated ion the C-O bond has high double-bond character while the C-S bond is almost

mercaptide in nature. The importance of the polar $O^+ = C$ bond is not clear.

(a) Binary Compounds

Binary compounds of monothioxanthate ligands are known for Cu(I)[38,39], Ag(I)[38], Hg(II)[40], Tl(I)[38,39] and Pb(II)[38]. In general, these complexes were obtained by preparing the ligand *in situ* from carbonyl sulphide gas and the appropriate alkoxide ion in solution. In most cases the solvent used was water[38,39] or ethanol[40], but attempts to prepare Fe(II) or (III), Ni(II), Co(II) or (III), Zn(II) and Cd(II) binary complexes in aqueous solution failed, with the reaction leading to decomposition and expulsion of COS.

[Cu(ROCOS)], where R = Me[39], Et[38,39] or Bu[39] and [Ag(ROCOS)] where R = Et[38] are all known. The Cu(I) complexes are prepared from Cu(II) chloride, and this reduction is attributed[38] to the formation of $(ROC(O)S)_2$, the oxidation product of monothioxanthate ions. Analogous disulphide oxidation products account for the reducing power of monothioacid ligands in general (see, for example, reference 10). [Cu(EtOCOS)] is formulated as a tetramer[38] from molecular weight measurements, and bidentate coordination of the ligand, with possible bridging through sulphur is suggested. Murphy and Winter[38] assigned bands around 1590 cm^{-1} and 1050 cm^{-1} as $\nu_{(CO)}$ and $\nu_{(CS)}$ in the potassium salts of a series of monothioxanthates, and they give values for [Cu(EtOCOS)] of $\nu_{(CO)}$ = 1665 cm^{-1} and $\nu_{(CS)}$ = 1020 cm^{-1}. Khwaja and Magee[39], however, follow earlier workers[43,44] in assigning a band at 700 cm^{-1} as $\nu_{(CS)}$, and give values of $\nu_{(CO)}$ = 1660-1680 cm^{-1} and $\nu_{(CS)}$ = 685-690 cm^{-1} for three [Cu(ROCOS)] complexes (R = Me, Et or Bu). The shift of $\nu_{(CO)}$ to higher frequency on complex formation suggests that the oxygen may be uncoordinated, or only weakly bound to the metal. The tetramers of

$[Cu(EtOCOS)]_4$ are probably held together by bridging sulphur atoms, with the role of the oxygen still unclear. $[Ag(EtOCOS)]$ proved too insoluble for molecular weight measurements[38], but by analogy with other Ag(I) monothioacid complexes[4,45] it is almost certainly oligomeric or polymeric in nature; the i.r. spectrum is consistent with sulphur-bridged coordination.

$[Hg(ROCOS)_2]$, R = Me or Et, was reported in 1937[40], prepared from HgO and RCO_2H in carbon disulphide as solvent. The complex was hydrolysed in water, and HgS was recovered. No spectroscopic or molecular weight data are available.

$[Tl(EtOCOS)]$ has been prepared by insertion of COS into $[Tl(EtO)]$[42] in ethanol, but the complex tends to decompose readily and recent attempts to obtain $[Tl(ArOCOS)]$ where Ar = aryl[41], have apparently been unsuccessful due to rapid decomposition of the product. The i.r. spectrum suggests that coordination, while possibly bidentate, is stronger through sulphur.

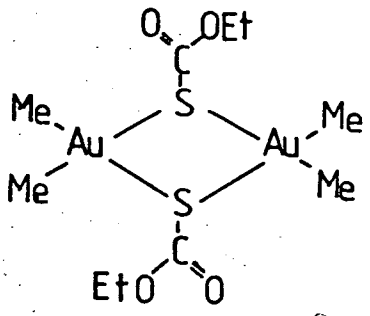
$[Pb(EtOCOS)_2]$ has been isolated[37] from aqueous solution, but decomposes on storage in organic solvents. The i.r. spectrum, which shows $\nu_{(CO)}$ at 1620 cm^{-1}, suggests little, if any, coordination through oxygen, but no further structural information is available.

(b) Compounds with Other Ligands

The Ru(II) species $[Ru(ROCOS)(PMe_2Ph)_4][PF_6]$, R = Me or Et, were isolated[34] by prolonged treatment of $[RuH(PMe_2Ph)_5][PF_6]$ with COS in methanol and ethanol solution respectively. Both species are presumably octahedral, with the monothioxanthate bidentate and chelated, and the i.r. spectrum is consistent with this.

The bis-pyridine adduct $[Ni(EtOCOS)_2(py)_2]$ has been prepared and characterised[38], although the binary species $[Ni(EtOCOS)_2]$ is apparently unobtainable. The i.r. spectrum suggests that the acid is coordinated through oxygen as well as sulphur. This is borne out by magnetic susceptibility measurements indicating a magnetic moment of 3.20 per nickel, and by the green colour, both suggesting strongly that the complex is octahedral, with the monothioxanthate acting as a bidentate chelate. The complex seems to be analogous to the green, paramagnetic, octahedral species discussed earlier[10,12,29,30].

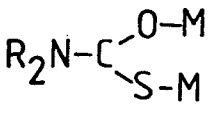
The Au(III) species $[Me_2Au(EtOCOS)]$ has been reported[35], prepared from $[Me_2AuBr]_2$ and KEtOCOS, and is formulated as a sulphur-bridged dimer (11), on the basis of i.r. evidence.



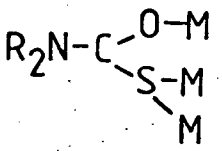
(11)

(iii) N,N-dialkylmonothiocarbamates R_2NCOS^-

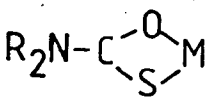
The N,N-dialkylmonothiocarbamates are the most widely studied of the monothioacids used as ligands. Unlike dithiocarbamates, which have a marked capacity to stabilise metals in high oxidation states and tend to form simple chelated complexes[2,47], monothiocarbamates generally coordinate with metals in low oxidation states and exhibit a wide range of bonding modes[48]:



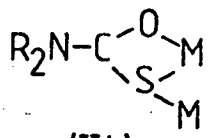
(Ia)



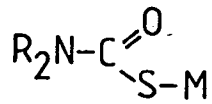
(Ib)



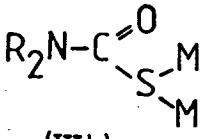
(IIa)



(IIb)



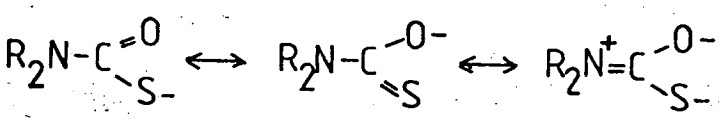
(IIIa)



(IIIb)

All of these modes of bonding have been proposed, and all but (Ia) and (IIIb) have been confirmed by X-ray structural analysis (see below for discussion of examples and references).

Like the monothioxanthate ion, the monothiocarbamate ion can be represented as a hybrid of three canonical forms:



A B C

Some workers[49,50] have suggested, on the basis of ligand dimensions arrived at in X-ray structure determinations on monothiocarbamate complexes, that resonance form A is more important for monothio- than for dithiocarbamates, i.e. the sulphur has a high mercaptide character with the ligand exhibiting short C-O distances (1.21 - 1.25 Å) and longer C-S (1.75 - 1.78 Å) and C-N (1.36 - 1.37 Å) than in comparable dithiocarbamate complexes. However, in the case of a chelated ligand where no bridging is present[49], this tendency is apparently less pronounced, with C-O (1.283(7)Å), C-S (1.735(6)Å) and C-N (1.342(7)Å) distances suggesting that canonical forms B and C are still important. A degree of double-bond character in the C-N bond is also suggested by i.r. spectra, with a stretching mode assigned as a mixture of $\nu_{(CO)}$

and $\nu_{(CN)}$ appearing characteristically between 1510 cm^{-1} [49] and 1660 cm^{-1} [51]. Several workers have argued that high values within this range for $\nu_{(CO)(CN)}$ indicate uncoordinated oxygen, but structural work[49] and a recent review of i.r. data[48] have shown that this can be misleading.

(a) Binary Compounds

Binary monothiocarbamate complexes are known for Ti(IV)[52], Mo(II)[54], Fe(II)[55] and Fe(III)[54,55,97], Co(II)[49], Ni(II)[56,57,58,59,60,98], Cu(I)[61,62,63,64], Ag(I)[45,63,64], Zn(II)[65], Cd(II)[65], Hg(II)[65] and Tl(I)[42]. In general the monothiocarbamate ligands are prepared as their secondary ammonium salts $[R_2NH_2][R_2NCOS]$ by treating the appropriate secondary amine with carbonyl sulphide, often in situ without isolating the salt.

The eight-coordinate Ti(IV) species $[Ti(Et_2NCOS)_4]$ has been prepared[52] and its structure determined by X-ray crystallography. It was prepared by insertion of COS into the Ti-N bonds of $[Ti(Et_2N)_4]$, and exhibits slightly distorted dodecahedral coordination (12). This represents an interesting departure from the pattern of coordination

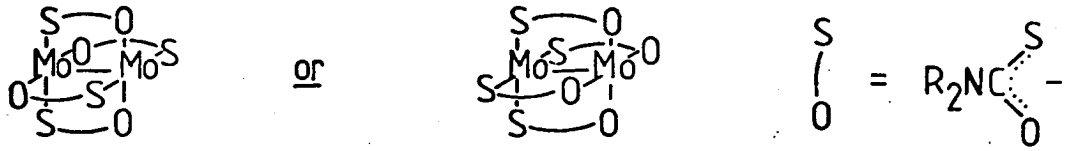
$\left(\begin{matrix} O \\ S \end{matrix}\right.$ = R_2NC (O, S) -

(12)

predicted by Orgel's Rule, which states[66] that the eight coordinated atoms in a dodecahedral complex fall into two sets, an elongated tetrahedron (the A sites) and a flattened tetrahedron (the B sites). In a d^0 system, such as Ti(IV), the stronger π-donors are expected to occupy the B sites, to achieve the most favourable interaction with the d

orbitals on the titanium. However, the oxygen and sulphur atoms in this example do not sort in this way, although the Ti-O and Ti-S bonds are significantly shorter at the B sites than at the A sites. The observed coordination may be due to weak interligand interactions between neighbouring sulphurs.

The Mo(II) complex $[Mo_2(C_4H_8NCOS)_4]$ is known[54], and is formulated as a dimer on the basis of its mass spectrum, with a proposed structure (13) of the molybdenum acetate type (cf. $[Mo_2(PhCOS)_4]$[5]). This is the only case so far where bidentate bridging by a monothiocarbamate ligand



(13)

is proposed, without additional bridging through the sulphur. Attempts to obtain Mo(III) and Mo(IV) complexes, analogous to known dithiocarbamate species, have been unsuccessful, illustrating the inability of the strongly reducing monothioacid ligands to form stable complexes with metals in high oxidation states.

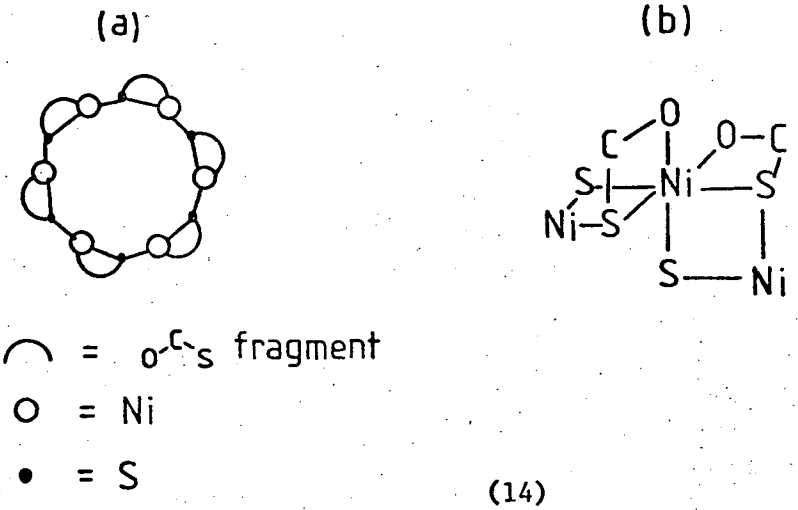
$[Fe(Me_2NCOS)_2]$[55] and $[Fe(R_2NCOS)_3]$, R = Me[54,55,97], Et[97] or n-Pr[97], or R_2 = C_4H_8 [54,97] or C_5H_{10} [54,97] have all been reported. The Fe(II) species is formulated as $[Fe(Me_2NCOS)_2]_n$ [55], and an oligomeric or polymeric structure, involving bidentate coordination with bridging through the sulphur, seems most likely. The complex is air-sensitive and readily converts to $[Fe(Me_2NCOS)_3]$. It was initially synthesised from the Fe(0) compound $Fe_2(CO)_9$ using $(Me_2NCOS)_2$ which was reduced

by the Fe(0)/Fe(II) oxidation couple to form the ligand. Alternatively, treatment of $FeCl_2$ with a stoichiometric amount of $[Me_2NH_2][Me_2NCOS]$ yielded the same species. $[Fe(R_2NCOS)_2]$, R = C_4H_8 or C_5H_{10}, has been reported as a transient species produced on treating $FeCl_2$ with R_2NCOS^-, but no structural data are available. The Fe(III) complexes were obtained by treating $FeCl_3$ with the appropriate monothiocarbamate salt[54,55,97]. $[Fe(Me_2NCOS)_3]$ can also be obtained from $[Fe(Me_2NCOS)_2]_n$ in the presence of sulphur or selenium, and on thermolysis at 220°C, the process is reversed and the Fe(II) species is recovered in 80% yield[55] together with the formation of $(Me_2NCOS)_2$. Here the monothiocarbamate ligand is acting as a reducing agent in contrast to the use of the disulphide as an oxidising agent in the preparation of the Fe(II) species. $[Fe(Me_2NCOS)_3]$ is formulated as a monomer from its mass spectrum and from molecular-weight measurements. It is a high-spin complex ($\mu_{eff.}$ = 6.11[55] or <u>ca</u> 5.4[54]) unlike the Fe(II) dithiocarbamates, which lie at the cross-over point between high- and low-spin states[68]. This suggests that the monothiocarbamates have lower ligand-field strengths than the dithiocarbamates. However, in a recent variable-temperature magnetic study of all the known Fe(III) monothiocarbamates[97], all but $[Fe(C_4H_8NCOS)_3]$, which is high-spin at all temperatures between 77K and 330K, exhibited a spin equilibrium analogous to that found in the dithiocarbamates. Apparently both mono- and dithiocarbamates of Fe(III) exhibit much faster interconversion of spin states than other Fe(III) complexes. Bidentate, chelated coordination of the monothiocarbamate ligands is proposed for all the Fe(III) complexes on the basis of i.r. spectra.

Co(II) species formulated as polymers $[Co(R_2NCOS)_2]_n$ are reported[49] to be readily formed, in contrast with the behaviour of Co(II) with dithiocarbamates and indeed with dithioacids in general (see earlier discussion on $[Co(PhCOS)_2]_2$). No full details of the preparation or

characterisation of $[Co(R_2NCOS)_2]_n$ species are available, however.

Ni(II) complexes with monothiocarbamate ligands have been widely studied. Complexes of empirical formula $[Ni(R_2NCOS)_2]$ are known for R = Me[56,58], Et[56,58], n-Pr[56,57,58,59,70] or n-Bu[56,58,59,60] and where R_2 = C_4H_8 [56,58,59] or C_5H_{10} [56,58,59]. A cyclic, oligomeric structure has been proposed[56] for all of the known complexes, and X-ray structure determinations for $[Ni(Pr_2NCOS)_2]_6$ [70] and $[Ni(Bu_2NCOS)_2]_6$ [60] have confirmed that they are hexamers (14a) with bidentate ligands bridging through sulphur to give a cis-octahedral configuration about the nickel atoms (14b). Magnetic measurements[56,59] indicate that the complex is paramagnetic,

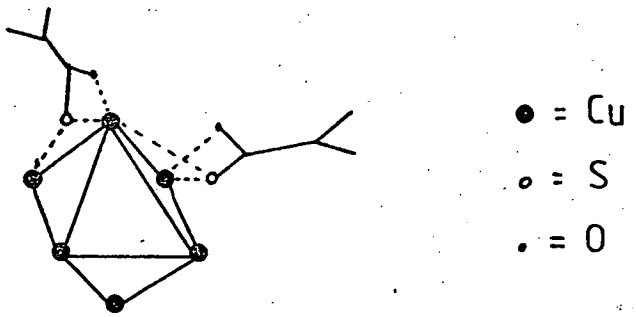


(14)

as expected for octahedral Ni(II), and the molecular weight approaches that of a hexamer in concentrated solutions, with breakdown of the cyclic units on dilution. A recent study[98] of the behaviour of $[Ni(R_2NCOS)]_n$, R = Pr or Bu, in very dilute benzene solutions reveals, from molecular-weight studies and absorption spectra, that under these conditions an equilibrium exists between a low-spin, square-planar monomer and a high-spin dimer, probably containing five-coordinate Ni(II). The difference between the structures found for $[Ni(R_2NCOS)_2]_6$ and that found for $[Ni(PhCOS)_2.0{\cdot}5\ EtOH]_2$[9], which exhibits no bridging via sulphur illustrates the higher mercaptide nature of the sulphur in the monothiocarbamates.

$[Pd(R_2NCOS)_2]_n$, where $R_2 = C_4H_8$ or C_5H_{10}, is reported[48] as the product when $[PdCl(C-N)]_2$, where C-N = benzylideneaniline-2-C,N or N,N-dimethylbenzylamine-2-C,N, or $K_2[PdCl_4]$, is reacted with the appropriate monothiocarbamate salt. The i.r. spectra suggest that there may be both monodentate sulphur-bonded ligands and bidentate ligands in these complexes (cf. $[Pt(PhCOS)_2]_n$ [12] discussed earlier) but the complexes were too insoluble for further characterisation.

The coinage metal complexes $[Cu(R_2NCOS)]$ and $[Ag(R_2NCOS)]$ have been prepared where R = Me, Et, n-Pr, n-Bu, i-Bu and iso-amyl[64]. The Cu(I) complexes are prepared from Cu(II) sulphate, illustrating again the reducing power of monothioacid ligands. All these complexes are formulated as hexamers and this has been confirmed in the solid state for $[Cu(Pr_2NCOS)]_6$ [62] and $[Ag(Pr_2NCOS)]_6$ [45] by X-ray analysis. In both structures, the metal atoms form an almost regular octahedron, with a ligand positioned above the centre of each of six faces, each ligand bound to three metal atoms (15).



(15)

Two opposite faces have no ligand associated with them. In these structures, unlike the $[Ni(R_2NCOS)]_6$ hexamers, the ligands are not chelated and this seems to be a function of metal-atom size, with the large atoms of the coinage metals forcing the monothiocarbamate to assume an entirely bridging mode of coordination. The mixed-metal complexes of formula $[CuAg(R_2NCOS)Et_2NCOS)]_3$ where R = Me or Et,

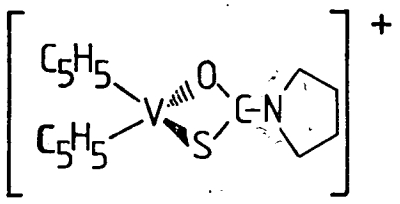
have recently been prepared[63] from $[Cu(R_2NCOS)]_6$ and $[Ag(Et_2NCOS)]_6$. Both complexes are said to have a ligand-bridged hexameric cluster structure similar to that of the $[M(Pr_2NCOS)]_6$ complexes. Molecular-weight measurements indicate that $[CuAg(Et_2NCOS)_2]_3$ is trimeric in methylene chloride solution, while the average degree of association for $[CuAg(Me_2NCOS)(Et_2NCOS)]_3$ was measured as 2.2.

The complexes $[M(R_2NCOS)_2]$ have been reported[65] where M = Zn, Cd or Hg and $R_2 = C_4H_8$ or C_5H_{10}. The solubility of these species varies with R, and the molecular weights measured in solution are concentration-dependent, though the effect is not so pronounced as for the Ni(II) complexes[56]. On the basis of i.r. spectra, it is proposed that the Zn(II) and Cd(II) complexes involve bidentate, bridging ligands which may be chelated, while in $[Hg(C_4H_8NCOS)]_n$ the monothiocarbamate is bound only through sulphur, possibly bridging adjacent metal centres (cf. $[Hg(PhCOS)_2]$ [4] discussed earlier).

$[Tl(R_2NCOS)]$ complexes are known[42] where R = Et or $R_2 = C_5H_{10}$. Both are apparently dimeric in solution and probably polymeric in the solid state. The i.r. spectra are consistent with some kind of bidentate bridging structure, but no further data are available.

(b) Compounds Containing Other Ligands

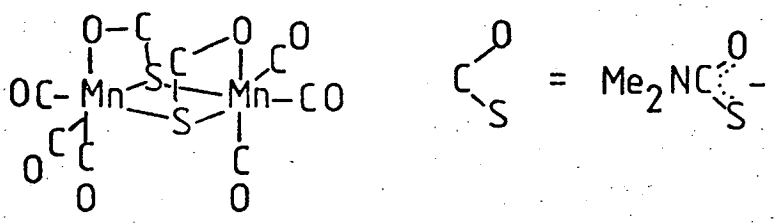
The V(IV) and V(III) complexes $[(\eta^5\text{-}C_5H_5)_2V(C_4H_8NCOS)]\ BF_4$ and $[(\eta^5\text{-}C_5H_5)_2V(C_4H_8NCOS)]$ have been studied electrochemically[71]. The V(IV) complex was prepared from $[(C_5H_5)_2VCl_2]$ and $C_4H_8NCOS^-$, and structure (16) is proposed. The neutral V(III) species was produced by electrochemical reduction of the cation, and is apparently quite stable in the absence of oxygen. The same tetrahedral structure is



(16)

proposed as for the cation, but no detailed spectroscopic or structural data are available.

The Mn(I) complex $[Mn(CO)_3(Me_2NCOS)]_2$ has been prepared[72] from $Mn(CO)_5Br$ and $[Me_3Sn(Me_2NCOS)]$[73]. The reaction takes place at room temperature in ether, and the use of $[Me_3Sn(R_2NCOS)]$ species as starting materials giving access to monothiocarbamate-carbonyl species under mild conditions is advocated. The Mn(I) complex is formulated as a dimer (17) on the basis of the carbonyl stretching modes observed in the i.r. spectrum.



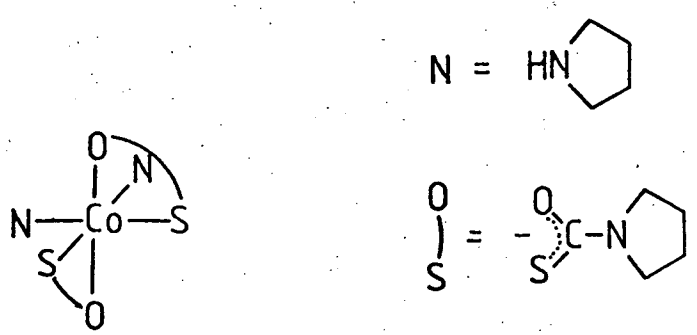
(17)

The Fe(II) complex $[Fe(Me_2NCOS)_2(bipy)]$ has been prepared[55] by treating either $[Fe(Me_2NCOS)_2]_n$ or $[Fe(Me_2NCOS)_3]$ with 2,2'-bipyridyl in benzene; $(Me_2NCOS)_2$ was formed quantitatively in the latter case. The i.r. spectrum is consistent with the bidentate, chelated coordination that would be expected in a monomeric, octahedral complex and the complex

is high-spin (μ_{eff} = 5.34 at ambient temperature). The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2C\ell]$ with $C_4H_8NCOS^-$ yielded the complex $[(C_5H_5)Fe(CO)_2(C_4H_8NCOS)]$[54]. Coordination of the monothiocarbamate is thought to be unidentate through sulphur, although in the dithiocarbamate analogues[98] the carbamate ligand forms a chelate ring, with the expulsion of a molecule of carbon monoxide. That this does not happen in the monothiocarbamate case is a reflection of the poorer donor properties of oxygen as against sulphur, and may also be a function of the smaller chelate bite of the ligand compared with dithiocarbamates.

The cationic Ru(II) complex $[Ru(Me_2NCOS)(PMe_2Ph)_4]^+$ has been prepared[34] by reaction of $[RuH(PMe_2Ph)_5][PF_6]$ with carbonyl sulphide in a mixture of ethanol and dimethylamine, and the monothioformate species $[Ru(HCOS)(PMe_2Ph)_4]^+$ also reacts with dimethylamine to give the monothiocarbamate complex. The monothioacid ligand is presumably coordinated as a bidentate chelate to give octahedral Ru(II).

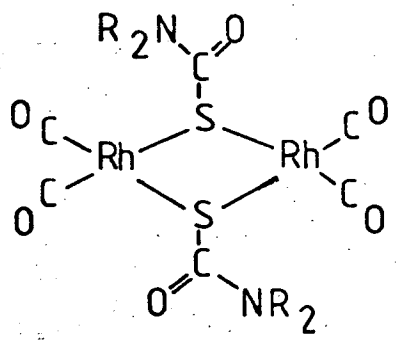
The first monothiocarbamate complex to be unambiguously assigned a structure containing simple chelated acid ligands was $[Co(C_4H_8NCOS)_2(C_4H_8NH)_2]$[49]. The X-ray structure of this complex reveals octahedral coordination about the metal, with the Co-O and Co-S bonds intact (cf. $[Zn(C_5H_{10}NCOS)_2(C_5H_{10}NH)_2]$[50]) with stereochemistry as shown in diagram (18).



(18)

Most complexes of Co(II) with S-donor ligands are tetrahedral, but in this case both the donor atoms of the acid have remained coordinated, although the long Co-S (2.584(2)Å) and Co-O (2.157(4)Å distances show that the acid ligand is fairly weakly bound, consistent with the low affinity of octahedral Co(II) for sulphur ligands and with the poor donor ability of oxygen.

When the yellow solution prepared by treating hydrated $RhCl_3$ with carbon monoxide in ethanol was treated with carbonyl sulphide in the presence of a secondary amine, red crystalline products of formula $[Rh(CO)_2(R_2NCOS)]$ were obtained[51], where R = Et or R_2 = C_4H_8 or C_5H_{10}. The compounds were diamagnetic and were dimeric in chloroform solution. The proposed structure (19) is analogous to the chloride-bridged dimer



(19)

$[Rh(CO)_2Cl]_2$[75] and it is assigned on the basis of the carbonyl stretches in the i.r. spectrum, while the monothiocarbamate modes are consistent with unidentate sulphur coordination. When the complexes were treated with excess secondary amine, crystalline products were recovered and in the case of $[Rh(CO)_2(C_4H_8NCOS)]/C_4H_8NH$ this product has been characterised as $[C_4H_8NH_2][Rh(CO)_2(C_4H_8NCOS)_2]$ with a square-planar anion containing cis-carbonyls and acid groups unidentate through sulphur. Treatment of $[Rh(CO)_2(Et_2NCOS)]$ with triphenylphosphine yields $[Rh(CO)(PPh_3)_2(Et_2NCOS)]$ which is assigned a square-planar

structure with trans-phosphines, by analogy with a series of Pd(II) complexes[58] discussed later. The complex $[Rh(CO)(PPh_3)_2(C_5H_{10}NCOS)]$ has also been made, by reacting $[RhCl(CO)(PPh_3)_2]$ with $C_5H_{10}NCOS^-$ [48] and it too is assigned a trans stereochemistry.

Several series of octahedral Ni(II) complexes of the form $[Ni(R_2NCOS)_2(amine)_2]$ are known. Complexes of the type $[Ni(R_2NCOS)_2(py)_2]$ where R = Me[56], Et[56], n-Pr[56,57,98], n-Bu[56,98] or R_2 = C_4H_8 [56,58], C_5H_{10}[56], are prepared by treating $[Ni(R_2NCOS)_2]_n$ [56] with pyridine. On heating, these complexes lose pyridine quantitatively to yield the parent $[Ni(R_2NCOS_2]_n$ [56]. Magnetic measurements, i.r. and electronic spectra indicate that these adducts are paramagnetic, octahedral Ni(II) species, monomeric in solution, with the monothiocarbamate coordinated as a chelate through both oxygen and sulphur. It seems that the base breaks down the bridging interactions which bind the cyclic $[Ni(R_2NCOS)_2]_n$ oligomers together, but does not rupture the Ni-O bonds (cf. $[Ni(PhCOS)_2(py)_2]$[29]. In a wider study of the reaction of $[Ni(R_2NCOS)_2]_n$ with amines[76], where $[Ni(Me_2NCOS)_2]_n$ and $[Ni(Pr_2NCOS)_2]_6$ were reacted with a range of primary and secondary amines, it was concluded from electronic spectra that secondary amines unhindered at the α-carbon gave trans-octahedral adducts, while α-hindered secondary amines gave diamagnetic species which may be planar with the monothiocarbamate unidentate, or may be pseudo-octahedral with a very weak ligand field allowing spin pairing in the ground state. Primary amines, however hindered, gave the characteristic green octahedral species identified as bis-amine adducts with bidentate monothiocarbamates. Straight-chain primary amines, however, gave blue octahedral complexes which may be tetrakis-amine adducts with the monothiocarbamates unidentate. A more recent study carried out using very dilute solutions[98] has shown that the addition of unidentate amines to $[Ni(R_2NCOS)_2]_n$ is stepwise with

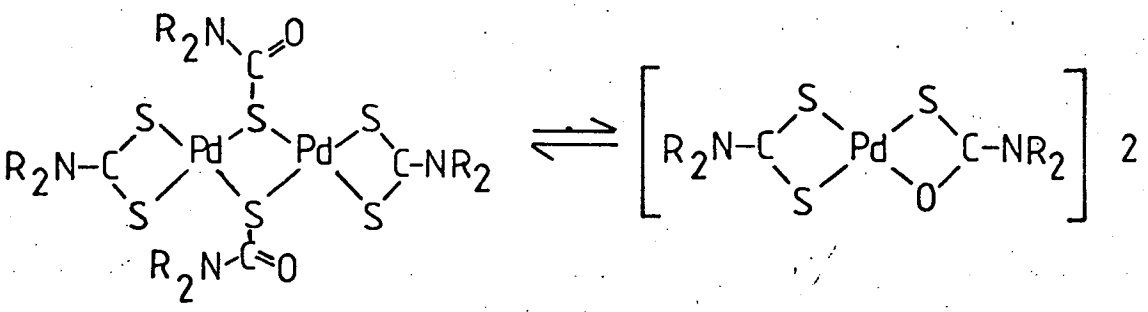
initial formation of a five-coordinate paramagnetic species. Measurements of the enthalpy of base addition suggest that in these complexes the Ni(II) is a stronger Lewis acid centre than in the analogous dithiocarbamate systems, and this may account for the greater tendency to polymerise. In the reaction of $[(\eta^5\text{-}(C_5H_5)Ni(PBu_3)(SH)]$ with alkyl cyanates RNCO, where R = Me, Et, Ph or cyclo-C_6H_{11}, the species $[(C_5H_5)Ni(PBu_3)(R_2NCOS)]$ is produced[77]. This is analogous to reactions with alkyl thiocyanates (RNCS) to give dithiocarbamates. The acid ligands are apparently unidentate through sulphur, giving four-coordinate Ni(II), but no further data are available.

The complex $[C_4H_8NH_2]_2[M(C_4H_8NCOS)_4]$, where M = Pd or Pt, can be isolated[58] from reaction mixtures containing $PdCl_2$ or $H_4(PtCl_6)$, carbonyl sulphide and pyrrolidine. The most likely stereochemistry in each case is square-planar with the monothiocarbamate ligands unidentate through sulphur, and the low $\nu_{(CO)(CN)}$ values reported may be attributable to hydrogen-bonding of the uncoordinated oxygen to the secondary ammonium ion.

The trans isomers of $[Pd(R_2NCOS)_2(PPh_3)_2]$ are known[58], where R = Me, Et or Bu; R_2 = C_4H_8 or C_5H_{10}, and cis-$[M(C_4H_8NCOS)_2(PPh_3)_2]$ is known[54] where M = Pd or Pt. The trans complexes were prepared by adding triphenylphosphine to a reaction mixture containing $PdCl_2$, carbonyl sulphide and the appropriate secondary amine. The dimethylphenylphosphine adduct $[Pd(C_4H_8NCOS)_2(PMe_2Ph)_2]$ was made in a similar way and its hydrogen-1-n.m.r. spectrum confirms the trans stereochemistry assigned to the series. In all the complexes, the monothiocarbamate is unidentate through sulphur. The cis complexes were prepared[54] from cis-$[MCl_2(PPh_3)_2]$ and $C_4H_8NCOS^-$, and they exhibit the same type of acid coordination.

A series of Pd(II) monomers involving bidentate chelated

monothiocarbamate ligands has been prepared[96], and the complexes, of formula $[Pd(az)(R_2NCOS)]$, where az = azobenzene-2-C,N and R = Me or $R_2 = C_4H_8$, C_5H_{10}, are monomeric in solution. The same workers have prepared[96] mixed mono- and dithiocarbamate Pd(II) complexes formulated as dimers in the solid state: $[Pd(R_2NCOS)(R'_2NCS_2)]_2$, where R = Ph, Me or $R_2 = C_4H_8$, C_5H_{10} and R' = Et, Bu or Ph. The dimers contain unidentate monothiocarbamate ligands bridging through sulphur, and bidentate dithiocarbamate. In solution, dissociation into monomers is proposed (20) on the basis of n.m.r. studies.



(20)

Tertiary phosphine adducts of Cu(I)[63,78] and Ag(I)[63] monothiocarbamates have been prepared by treating $[M(R_2NCOS)]_6$, R = Me, Et, with triphenylphosphine or methyldiphenylphosphine. In the case of the Cu(I) species, formed from $[Cu(R_2NCOS)]_6$, the products were characterised as $[Cu(R_2NCOS)_2(PR'Ph_2)_{3 \text{ or } 4}]$ where R' = Me or Ph. All the species dissociate in solution and, in the presence of excess tertiary phosphine, the coordinatively saturated $[Cu_2(R_2NCOS)_2(PR'Ph_2)_4]$ predominates. When $[CuAg(R_2NCOS)(Et_2NCOS)]_3$, R = Me or Et, was treated with the phosphines[63], $[CuAg(R_2NCOS)(Et_2NCOS)(PR'Ph_2)_{3 \text{ or } 4}]$ was formed and in solution this exists as a mixture of mixed-metal complexes, some with bridging monothiocarbamate ligands. The addition of excess phosphine produced $[Cu_2(R_2NCOS)_4(PR'Ph_2)_2]$ and $[Ag(R_2NCOS)(PR'Ph_2)_2]$ species.

The Au(I) complexes $[Au(R_2NCOS)(PPh_3)]$ are known[48] where R = Me, Ph or $R_2 = C_5H_{10}$, and the i.r. spectra are consistent with unidentate coordination through sulphur, as in the analogous dithiocarbamates.

$[Zn(C_5H_{10}NCOS)_2(C_5H_{10}NH)_2]$ was first prepared by Krankovits et al.[58] and its structure has been determined by X-ray crystallography[50]. Unlike the Co(II)[49] and Ni(II)[76] monothiocarbamate adducts with secondary amines, the Zn(II) complex exhibits no metal-oxygen coordination, but is tetrahedrally coordinated to two amines and two unidentate monothiocarbamates, bound through sulphur. Short Zn-S distances (2.314(3)Å and 2.294(3)Å) indicate strong coordination of the ligand (cf. Co(II) case[49]) and the sulphur has fairly high mercaptide character (C-S = 1.75(1)Å). The low value of $\nu_{(CO)(CN)}$ in the i.r. spectrum (1450, 1550 cm^{-1}) can be accounted for by hydrogen-bonding of the uncoordinated oxygen to the amine nitrogen.

(iv) Dialkylmonothiophosphinates R_2POS^-

Metal complexes of dialkylmonothiophosphinates have not been very widely studied; for example, no monothiophosphinate complexes are known for the platinum metals, although the complexes of one or two metals, notably Co(II), Zn(II) and Cd(II) have been studied in detail.

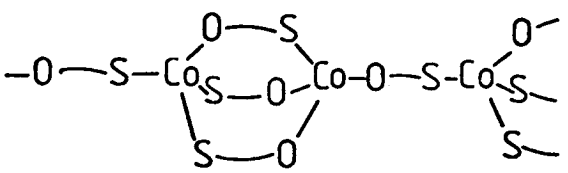
(a) Binary Compounds

Binary complexes with monothiophosphinate ligands are known for Mn(II)[79], Co(II)[17,80,81,82,83], Ni(II)[84,85], Cu(II)[86], Ag(I)[86], Zn(II)[17,80,81,82,87,88], Cd(II)[17,80,85], In(III)[17,80] and Ph(II)[80,86].

The reaction of manganese (II) acetate with R_2POSH, where R = Et or

Ph, leads to the formation of polymers[79], presumably of formula $[Mn(R_2POS)_2]_n$ with molecular weights ranging from 1850 to 7800, and a degree of association between 6 and 16. No details about coordination or bonding are available.

The Co(II) complexes $[Co(R_2POS)_2]$, where R = Et[17,80,81,82,83], n-Bu[82,83] or Ph[82,83], are known and their behaviour in solution[17,80,81] and their structures[82] have been studied in detail. These complexes all exhibit concentration-dependent association when dissolved in non-coordinating solvents, and solutions of $[Co(Et_2POS)_2]$ have high viscosities[17,80,81], corresponding to high molecular weights, even at low concentrations. Flow studies in benzene indicate the presence of discrete clusters held together by strong bonds, and stable monothiophosphinate bridges are postulated. Electronic spectra indicate that the Co(II) ions are tetrahedrally coordinated, and an X-ray structure analysis of $[Co(Ph_2POS)_2]$[82] confirms this, revealing a polymeric structure (21) in the solid state which is analogous to the linkage



(21)

found in polymeric $[Zn(R_2PO_2)_2]_n$ species[89], and containing alternate CoO_3S and CoS_3O tetrahedra. In coordinating solvents, the polymeric structure is broken down; for example $[Co(Et_2POS)_2]_n$ dissolves in pyridine[80] to give the monomeric, octahedral species $[Co(Et_2POS_2(py)_4]$ with unidentate monothiophosphinate ligands.

$[Ni(R_2POS)_2]$ species are known with R = Me[84] or Ph[85], and the vibrational spectra for $[Ni(Me_2POS)_2]$ are apparently best accounted for by postulating a polymeric chain structure, but no further details are available.

$[Cu(Et_2POS)_2]$ and $[Ag(Et_2POS)]$ have also been prepared[86] and studied by vibrational spectroscopy. Examination of P-O and P-S modes suggests in both cases a polymeric chain structure containing linked MO_2S_2 units (M = Cu or Ag).

The Zn(II) and Cd(II) complexes $[M(R_2POS)_2]$, where M = Zn or Cd, R = Et[17,80,81,82], n-Bu[82], t-Bu[87] or Ph[82,85], are all known, and some $[Zn(R_2POS)_2]$ species are active antioxidants for hydrocarbons[88]. The complexes exhibit associative behaviour in non-coordinating solvents similar to that discussed earlier for the Co(II) complexes, and X-ray studies[82] on fibres and powders of $[Zn(Bu_2POS)_2]$ reveal a polymer with the same backbone structure as $[Co(Ph_2POS)_2]_n$ (21).

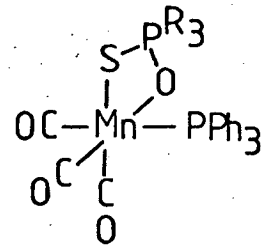
The In(III) complex $[In(Et_2POS)_3]$ exists as an octahedral monomer in solution[17,80], regardless of the coordinating ability of the solvent. This observation leads to the suggestion[17] that the degree of association observed in monothiophosphinate complexes is largely a matter of steric factors, arising from the geometry around the metal. In an octahedral complex the strain in a chelate ring is minimised, while in a tetrahedral complex, where the strain in a four-membered chelate ring is increased due to the greater bond angle at the metal, the formation of ligand bridges is preferred.

$[Pb(Et_2POS)_2]$[80,86] exhibits the familiar associative behaviour in solution[80] and a polymeric chain structure made up of linked PbO_2S_2 units has been proposed on the basis of vibrational spectra[86] (cf. Cu(II) and Ag(I) complexes).

(b) Compounds containing other ligands

Various Mo(V) and (VI) and W(VI) species have been reacted with Ph_2POSH[90,91] to give a range of monomeric products in which the monothiophosphinate ligands are bidentate: $[MoO_2Cl(Ph_2POS)]$[91], $[MoOCl(Ph_2POS)]$[90], $[WO_2(Ph_2POS)_2]$[91], $[WOCl_3(Ph_2(POS)]$[91], and a chloride-bridged dimer which is formed on heating $[MoO_2Cl(PhCOS)]$. In one Mo(VI) complex, $[MoOCl_3(Ph_2POS)]$[90], the monothiophosphinate is unidentate through sulphur. The complexes were characterised on the basis of e.s.r. parameters.

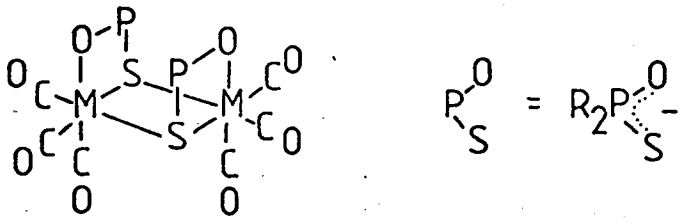
$M(CO)_5Br$, where M = Mn or Re, has been treated with monothiophosphinic acids R_2POSH, R = Et or Ph, to give the monomeric $[M(CO)_4(R_2POS)]$[92,94] or the dimeric $[M(CO)_3(R_2POS)]_2$[93,94]. The monomers are octahedral[92] with the monothiophosphinate bound as a bidentate chelate, and $[Mn(CO)_4(R_2POS)]$ reacts with triphenylphosphine to give a product which is assigned the structure (22).



(22)

Here, the phosphine has displaced a molecule of carbon monoxide rather than attack the Mn-O bond to give $[Mn(CO)_4(PPh_3)(R_2POS)]$ with a unidentate acid ligand, illustrating the stability of monothiophosphinate chelate rings in octahedral systems. In the $[M(CO)_3(R_2POS)]_2$ dimers, the monothiophosphinate ligands are again bidentate (i.r. evidence) and although detailed structural assignments are not available, it

seems reasonable to postulate structures (23) analogous to



(23)

those proposed for $[Mn(CO)_3(R_2NCOS)]_2$ dimers, with bridging through sulphur. $[Re(CO_3(R_2POS)]_2$ reacts with triphenylphosphine to give the monomer $[Re(CO)_3(PPh_3)(R_2POS)]$[93], and an excess of triphenylphosphine leads to the formation of $[Re(CO)_2(PPh_3)_2(R_2POS)]$ with bidentate monothiophosphinate, and $[Re(CO)_3(PPh_3)_2(R_2POS)]$ with the acid ligand unidentate. The formation of $[Re(CO)_3(Ph_2POS)]_2$ dimers has been carefully studied[94], with the isolation of intermediates, and the proposed mechanism is outlined as follows:

$Re(CO)_5Br$ + Ph_2POSH $\xrightarrow[-CO]{65^\circ}$ $[Ph_2P(OH)SRe(CO)_4Br]$ (with unidentate P-S-Re linkage)

$[Ph_2P(OH)SRe(CO)_4Br]$ $\xrightarrow[-CO]{65\text{-}80^\circ}$ $[Ph_2P(OH)S\ Re(CO)_3Br]$ (with $Ph_2P(OH)S$ acting as a bidentate ligand through S and O)

$[Ph_2P(OH)S\ Re(CO)_3Br]$ $\xrightarrow[-HBr\ \text{dimerisation}]{80^\circ}$ $[(Ph_2POS)Re(CO)_3]_2$

The coordination in the intermediates was elucidated from i.r. spectra and by isolating O-methylated products.

The reaction of zinc(II) carbonate with monothiophosphinic acids[95]

yielded basic compounds of formula $[Zn_4O(R_2POS)_6]$ with R = Et, n-Bu or Ph. An X-ray structure analysis of the n-butyl species revealed a central oxygen atom surrounded by a tetrahedron of zinc ions, with the edges of the tetrahedron bridged by bidentate monothiophosphinate ligands. The coordination around each Zn(II) centre could not be unambiguously determined due to the possibility of disorder in the structure.

(v) Summary

In general, the monothioacid ligands which have been studied to date show some fairly consistent patterns of behaviour. They do not share the tendency of dithioacid ligands, especially dithiocarbamates, to stabilise metals in high oxidation states[2], partly due to the reduction in the electron-donating power of the ligands on substituting oxygen for sulphur[54], and also due to the reducing power of the monothioacids, which are readily oxidised to form stable disulphides.

Bidentate monothioacids tend to form oligomeric or polymeric metal complexes by acting as bidentate bridges[9,39,54,82], by forming chelates which bridge *via* sulphur[60,72] or even by bridging three metal atoms[45,62] without chelation. The ability of monothioacids to form chelate rings seems to be largely a matter of the size[62] and coordination geometry[17] of the metal ion, with chelation most likely for the smaller metal ions and for octahedral or square-planar systems. Simple chelated monothioacid ligands are most often found in monomeric systems, notably those of Co(II)[6] and Ni(II)[12,29,38,56], where disruption by moderately strong Lewis bases of the bridging structure in an oligomeric binary compound has left the metal-oxygen bonds intact and an octahedral geometry results in systems which might be expected

to prefer tetrahedral or square-planar coordination with sulphur donors. However, monothioacids generally come lower in the spectrochemical series than the corresponding dithioacids, and form high-spin complexes not only with Ni(II) and Co(II) but also with Fe(II)[55] and Fe(III)[54,55]. Chelation is also found in cases where the oxygen donor is required to complete the coordination shell of, for example, ruthenium(II).

When monothioacids act as unidentate ligands they interact with most transition metals through the sulphur atom, which has a high mercaptide character in most cases, enabling it to act as pseudo-halide[26,32] and sometimes as a bridging ligand without any participation by the oxygen[4,12,22,34]. Unidentate monothioacids will form square-planar Ni(II)[12] and tetrahedral Co(II)[26] complexes, although here the influence of other donor ligands is clearly crucial.

CHAPTER 2

REACTIONS OF mer-$RuCl_3(PMe_2Ph)_3$ AND $RuCl_2(PPh_3)_3$ WITH AMMONIUM AND SODIUM MONOTHIOBENZOATES AND THE REACTIONS OF THE PRODUCTS WITH SOME MONODENTATE LEWIS BASES

2(i) Introduction

Extensive studies have been carried out[99-101] on the reaction of a wide range of Ru(II) and (III) tertiary phosphine and phosphite complexes with a variety of sodium dithioacid salts. In polar solvents, under reflux, compounds of the type cis-$Ru(S\text{-}S)_2(PR_3)_2$ are formed with $S\text{-}S^-$ = dithioacid ligand and PR_3 = tertiary phosphine, phosphinite etc., and some of these complexes, notably those containing dialkyldithiophosphinates, exhibit the phenomenon of facile optical isomerisation in solution, attributed to a solvent-assisted bond rupture mechanism[100]. The present work was begun in order to establish whether this pattern of behaviour extends to complexes containing monothioacid ligands, and the monothiobenzoate ligand in particular has been studied.

2(ii) Results and Discussion

(a) Reactions of mer-$RuCl_3(PMe_2Ph)_3$ and $RuCl_2(PPh_3)_3$ with ammonium and sodium monothiobenzoate

When mer-$RuCl_3(PMe_2Ph)_3$ and $RuCl_2(PPh_3)_3$ were gently refluxed in methanol or acetone with excess of sodium monothiobenzoate, or in methanol with ammonium monothiobenzoate, a product analysing for $Ru(PhCOS)_2(PR_3)_2$ (see Experimental section) was obtained in all instances*. In the i.r.

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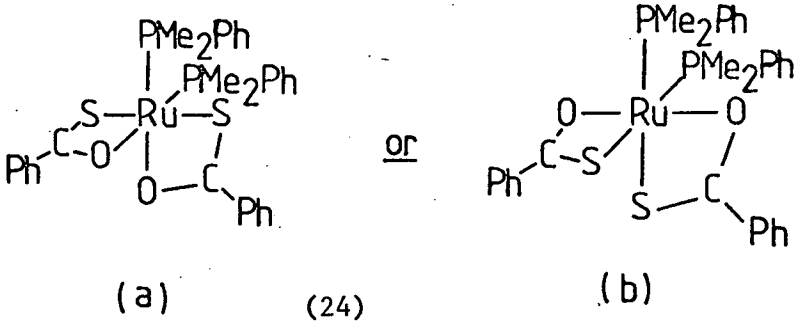
* However, the reaction of $RuCl_3(PMe_2Ph)_3$ with ammonium monothiobenzoate in acetone resulted in a product containing 3.3% nitrogen, which will be discussed later.

spectra of the two complexes (see Table 2.1), $\nu_{(CO)}$ is observed at 1470 cm^{-1} for $Ru(PhCOS)_2(PMe_2Ph)_2$ and at 1500 cm^{-1} for $Ru(PhCOS)_2(PPh_3)_2$, and $\nu_{(CS)}$ for both at 935 cm^{-1}. Comparison of these values with those observed for sodium monothiobenzoate ($\nu_{(CO)}$: 1500 cm^{-1} and $\nu_{(CS)}$: 960 cm^{-1}) indicates coordination through both oxygen and sulphur to give four-membered chelate rings (see reference 4, and discussion in Introduction, section (i)). Both complexes gave non-conducting solution in $CH_2C\ell_2$, and the mass spectrum of $Ru(PhCOS)_2(PMe_2Ph)_2$ shows a parent-ion peak at m/e = 652 (for ^{102}Ru), the molecular weight of the complex as formulated. Peaks at m/e = 137 and m/e = 138 show the loss of monothiobenzoate and dimethylphenylphosphine groups respectively.

The ^1H-n.m.r. spectrum of $Ru(PhCOS)_2(PPh_3)_2$ (see Table 2.2) is not very informative, since phenyl resonances from the monothiobenzoate and the triphenylphosphine are superimposed, but the $^{31}P-\{^1H\}$-n.m.r. spectrum shows a single peak at 59.87 p.p.m. (see Table 2.3), indicating the presence of a single species containing magnetically equivalent phosphines. The ^1H-n.m.r. spectrum of $Ru(PhCOS)_2(PMe_2Ph)_2$, on the other hand, is particularly interesting in view of the results previously found for $Ru(S-S)_2(PR_3)_2$ systems[99,100]. At ambient temperature (300K), a strong "pseudo-triplet" pattern is observed at 1.42δ, and a weaker 1:2:1 triplet at 1.57δ. A "pseudo-triplet" is a doublet with a broad band of intensity visible between the two peaks, and arises in the spectra of complexes containing two equivalent methyl-bearing tertiary phosphines which are coupled such that $\left|J_{PP'}\right| \geq \left|J_{PH} + J_{PH'}\right|$ i.e. where the coupling between the two phosphorus nuclei is large compared with the phosphorus-hydrogen coupling[100]. At low temperature (280K) the pseudo-triplet broadens, and at 260K two pseudo-triplets are observed at 1.32δ and 1.46δ. This type of behaviour was found[99] to be characteristic of <u>cis</u>-$Ru(S-S)_2(PMe_2Ph)_2$ systems and has been attributed

to the occurrence of a facile interconversion between two enantiomers in solution. The mechanism of the process is believed to involve rupture of the Ru-ligand bond trans to a phosphine (Scheme 2.1), such that at ambient temperature methyl groups a, b, c and d become equivalent. At lower temperatures the process is slowed down and the methyl groups are observed as two inequivalent pairs, a, c and b, d, which give rise to two pseudo-triplets in the ^{1}H-n.m.r. spectrum. The apparent equivalence of all the methyl groups is restored when the temperature is raised again and the rate of isomerisation becomes fast compared to the n.m.r. timescale. (It should be noted that free rotation about the Ru-P bond cannot make the methyl groups on a phosphine of this type equivalent to each other as the phosphorus atom is effectively a chiral centre when bonded to an asymmetrically coordinated metal ion.) The 1:2:1 triplet is unaffected by lowering of the temperature, apart from broadening due to increased viscosity, and it is attributed to the presence of a small amount of another isomer in which the phosphines are equivalent and trans to each other. Decoupling of the ^{1}H-n.m.r. spectrum leads to the collapse of the pseudo-triplet to a singlet at a frequency equivalent to a ^{31}P chemical shift of ca 38 p.p.m., and the 1:2:1 triplet collapses at ca 4 p.p.m. This is in agreement with the ^{31}P-{^{1}H}-n.m.r. spectrum (Table 2.3), which exhibits a strong singlet at 39.00 p.p.m. and a weaker signal at 4.57 p.p.m. Accordingly, the stereochemistry of $Ru(PhCOS)_2(PMe_2Ph)_2$ in solution can be assigned at this stage as a major species (24) containing equivalent cis-phosphines and a minor species containing trans-phosphines.



(a) (24) (b)

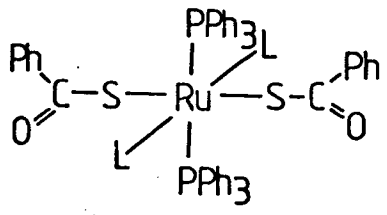
(b) Reactions of $Ru(PhCOS)_2(PR_3)_2$ compounds with monodentate Lewis bases

When the dithioacid complexes $Ru(S\text{-}S)_2(PR_3)_2$ were reacted with carbon monoxide, products of formula $Ru(S\text{-}S)_2(PR_3)(CO)$ were formed[99], with the carbonyl group taking the place of a phosphine. Only in the case of $Ru(R_2PS_2)_2(PMe_2Ph)_2$ was a product isolated in which both phosphines remained and a Ru-S bond was ruptured to give a unidentate dithiophosphinate ligand, namely $Ru(R_2PS_2)_2(PMe_2Ph)_2(CO)$. In the case of $Ru(PhCOS)_2(PR_3)_2$, however, the Ru-O bonds are expected to be more labile than either Ru-P or Ru-S bonds, and therefore products of the form $Ru(PhCOS)_2(PR_3)_2L_2$ were anticipated when the complexes were treated with a monodentate Lewis base, L.

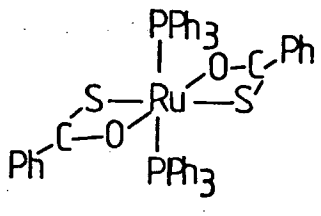
Thus, reaction of $Ru(PhCOS)_2(PR_3)_2$, $PR_3 = PPh_3$ or PMe_2Ph, with L = carbon monoxide, ammonia and diethylamine gave the expected product $Ru(PhCOS)_2(PR_3)_2L_2$ in each case, although $Ru(PhCOS)_2(PMe_2Ph)_2(NH_3)_2$ could not be isolated and was characterised from its n.m.r. spectra alone (see Experimental section). Each of the adducts isolated gave a non-conducting solution in CH_2Cl_2, and inspection of the $\nu_{(CO)}$ and $\nu_{(CS)}$ values observed in the i.r. spectra (Table 2.1) shows that in each case $\nu_{(CO)}$ has shifted to higher frequency. In $Ru(PhCOS)_2(PMe_2Ph)_2(CO)_2$ this increase in frequency is as much as

130 cm^{-1}, but in $Ru(PhCOS)_2(PMe_2Ph)_2(NHEt_2)_2$ it is only 25 cm^{-1}; this can be attributed to some hydrogen-bonding of the acid oxygen to coordinated amine groups (see Section 2(ii)c and compare with the i.r. spectra of $[Ni(MeCO_2)_2]\cdot 4H_2O$ [103] and $Pd(MeCO_2)_2(NHEt_2)_2$ [104] where hydrogen-bonding of the uncoordinated carboxylate oxygens to water and diethylamine respectively accounts for the lowering of $\nu_{asym}(CO_2)$.) The $\nu_{(CS)}$ frequency is shifted in each case some 20-30 cm^{-1} lower, and this indicates that in these adducts the Ru-O bonds have been broken, and the monothiobenzoate ligands are now coordinated in unidentate fashion through sulphur. The carbonyl stretching region in the i.r. spectrum of $Ru(PhCOS)_2(PPh_3)_2(CO)_2$ shows one $\nu_{(CO)}$ band at 1950 cm^{-1}, indicating <u>trans</u> carbonyl groups, while in $Ru(PhCOS)_2(PMe_2Ph)_2(CO)_2$ two $\nu_{(CO)}$ bands are observed at 2005 and 2025 cm^{-1}, indicating a <u>cis</u>-carbonyl arrangement.

The $^{31}P-\{^1H\}$-n.m.r. spectra of $Ru(PhCOS)_2(PPh_3)_2L_2$ in $CDCl_3$ show strong singlets at 46.30 p.p.m. (L = NH_3) and 42.83 p.p.m. (L = CO). These relatively small shifts from the position of the singlet in $Ru(PhCOS)_2(PPh_3)_2$ itself (59.87 p.p.m.) suggest that the Lewis base molecules are coordinated <u>cis</u> to the phosphines, which themselves remain trans and therefore equivalent. On this basis structure (25a) is proposed for $Ru(PhCOS)_2(PPh_3)_2L_2$ and structure (25b) for $Ru(PhCOS)_2(PPh_3)_2$. In the case where L = CO further evidence for



(a)

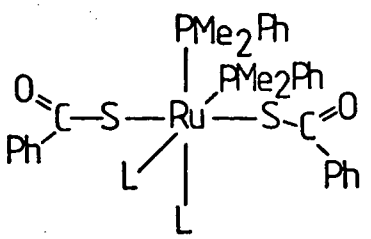


(b)

(25)

the correctness of this structure is obtained from the reaction of trans, trans-$RuCl_2(CO)_2(PPh_3)_2$ [105] with ammonium monothiobenzoate, which gives an isomer of $Ru(PhCOS)_2(PPh_3)_2(CO)_2$ with the same spectroscopic properties as the product obtained by treating $Ru(PhCOS)_2(PPh_3)_2$ with carbon monoxide.

The room-temperature ^1H-n.m.r. spectra of $Ru(PhCOS)_2(PMe_2Ph)_2L_2$, however, show a pseudo-triplet at 1.75δ (L = NH_3), 1.74δ (L = $NHEt_2$) and 1.60δ (L = CO). These patterns are unaffected by lowering the temperature, showing no sign of splitting. In the ^{31}P-{^1H}-n.m.r. spectra strong singlets are observed at 23.66 p.p.m. (L = NH_3), 22.32 p.p.m. (L = $NHEt_2$) and -10.79 p.p.m. (L = CO), a considerable shift, in the case of the carbonyl adduct, from the ^{31}P resonance (39.00 p.p.m.) observed for the cis-phosphine isomer of $Ru(PhCOS)_2(PMe_2Ph)_2$. This large change in the ^{31}P resonance position of the phosphines suggests that the Lewis bases are coordinated trans to the phosphines and this is in agreement with the cis stereochemistry of the carbonyl groups inferred from the i.r. spectrum for $Ru(PhCOS)_2(PMe_2Ph)_2(CO)_2$. On the basis of these spectroscopic studies, the structure (26) is proposed for the Lewis base adducts and (24a) for the cis isomer of $Ru(PhCOS)_2(PMe_2Ph)_2$.



(26)

Structure (26) has mirror symmetry about the RuP_2L_2 plane, which renders the methyl groups on each phosphine equivalent under all conditions.

Presumably the preference for trans stereochemistry in the triphenylphosphine complexes and for cis stereochemistry in those of dimethylphenylphosphine reflects both the steric constraints of the bulkier phosphine and the high trans influence of dimethylphenylphosphine.

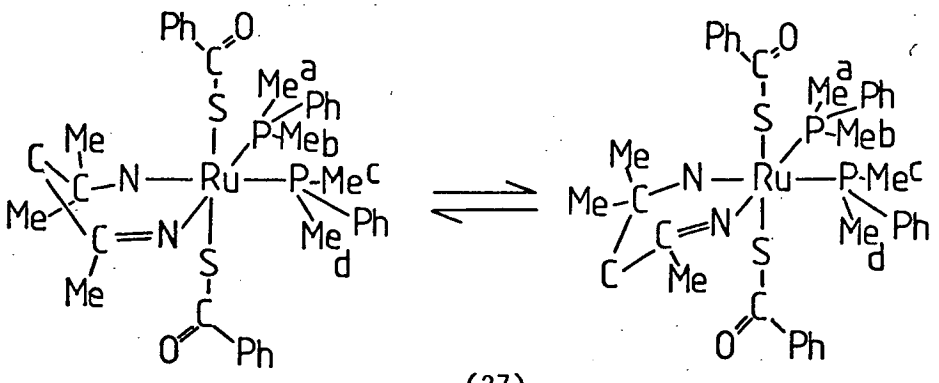
(c) The Reaction of mer-$RuCl_3(PMe_2Ph)_3$ with ammonium monothiobenzoate in acetone.

When mer-$RuCl_3(PMe_2Ph)_3$ was reacted with ammonium monothiobenzoate in acetone, either at ambient temperature or under reflux, a product analysing for 3.3% nitrogen was obtained in over 70% yield. No unequivocal formula or structure could be assigned on the basis of chemical and spectroscopic evidence alone, and an X-ray crystal structure analysis was therefore carried out (see Section 2(iii)), which revealed that the complex was $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$, containing the unusual 4-amino-2-imino-4-methylpentane molecule acting as a bidentate ligand. The complex gave a non-conducting solution in CH_2Cl_2 and was shown by osmometric molecular weight measurements to be monomeric in $CHCl_3$. In the mass spectrum, the parent-ion peak of the compound was not observed as expected at m/e = 766(^{102}Ru), but at m/e = 652(^{102}Ru) the molecular weight of $Ru(PhCOS)_2(PMe_2Ph)_2$, indicating the ready loss of the imino-amino ligand. The rest of the mass spectrum for m/e > 100 is essentially the same as that of $Ru(PhCOS)_2(PMe_2Ph)_2$, exhibiting loss of the monothiobenzoate and dimethylphenylphosphine ligands, but for m/e < 100 additional peaks are observed at m/e = 97, 58, 42 and 15. Comparison with the mass spectrum of $[Ni(HNCMeCH_2CMe_2NH_2)_2][PF_6]_2$ (prepared in reference 106, but mass spectrum not quoted) suggests that these peaks are

characteristic of the imino-amino ligand, and a fragmentation pattern is proposed (Scheme 2.2). No peak is observed at m/e = 114, the molecular weight of the ligand, illustrating the known instability of compounds containing imine groups, which readily rearrange or polymerise[107].

In the i.r. spectrum of the complex (see Table 2.1) the characteristic monothiobenzoate modes, $\nu_{(CO)}$ and $\nu_{(CS)}$, are observed at 1530 cm^{-1} and 935 cm^{-1} respectively, indicative of the presence of unidentate S-bonded monothiobenzoate groups. The low value of $\nu_{(CO)}$ compared with that in other S-bonded monothiobenzoate complexes is attributed to some hydrogen-bonding interaction between the carbonyl oxygen and the coordinated primary amine group of the imino-amino ligand, and this is confirmed by the O-N(amine) distances found in the X-ray structure (see discussion in Section 2(iv)). Bands observed between 3040 and 3300 cm^{-1}, at 1660 cm^{-1} and at 1587 cm^{-1} are assigned as the N-H stretching modes of the coordinated primary amine, the C=N stretch of the coordinated imine and the $-NH_2$ deformations of the amine respectively, by comparison with the values reported for the i.r. spectrum of $[Ni(HNCMeCH_2CMe_2NH_2)_2][PF_6]_2$[106].

The ^{1}H-n.m.r. spectrum of the complex (Table 2.1) at ambient temperature shows a pair of doublets arising from the methyl groups on two magnetically inequivalent phosphines, and as the temperature is lowered, each signal broadens and then splits into two doublets indicating that the methyl groups on each phosphine have now become inequivalent on the n.m.r. timescale. Examination of the stereochemistry of the complex (as revealed by the X-ray study and shown schematically in (27)) indicates that the rapid inversion, expected at room temperature, of the puckered six-membered ring formed by the chelated imino-amino ligand will render the methyl groups on <u>each</u> phosphine



(27)

equivalent, while at lower temperatures the two conformers will be "frozen out" as the ring inversion process slows down. A ^{31}P decoupling study shows that the doublet at 1.43δ collapses to a singlet when irradiated at a frequency equivalent to a ^{31}P chemical shift of ca 23 p.p.m., and the doublet at 1.86δ collapses when irradiated at ca 16 p.p.m. Accordingly, in the $^{31}P-\{^{1}H\}$-n.m.r. spectrum, an AB pattern is observed centred at 19.9 p.p.m. with δ(PP) = 251.7Hz and $J_{(PP)}$ = 32.9 Hz. The magnitude of the $J_{(PP)}$ value suggests a cis configuration of phosphines[108], subsequently confirmed by the X-ray study. The ^{1}H-n.m.r. spectrum also contains resonances arising from the imino-amino ligand at 1.06δ (geminal methyls), 1.58δ (methyl group on the imine carbon) and 2.31δ (methylenic protons), which are assigned by comparison with the ^{1}H-n.m.r. parameters reported for $[Ni(HNCMeCH_2CMe_2NH_2)_2][PF_6]_2$[106]. The relative intensities of the peaks are approximately 12:5:2, and the anomalously large value for the geminal methyl resonance may arise from its superposition on the resonances of broadened amine protons. A small broad resonance at 5.80δ is in the right position for the proton of the coordinated imine group.

To try to establish the mechanism of formation of the imino-amino ligand, a number of attempts were made to synthesise

$Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$ by alternative routes. For example, reaction of mer-$RuCl_3(PMe_2Ph)_3$ with sodium monothiobenzoate and acetone in the presence of ammonium ions gave the desired product in a high yield, but when $Ru(PhCOS)_2(PMe_2Ph)_2$ was treated with ammonium ion in acetone, only the starting material was recovered. In the synthesis of previous complexes containing coordinated 4-amino-2-imine-4-methyl-pentane groups the starting material has contained coordinated amines[106] or has been treated with ammonia *in situ*[109] so that a metal-ammine complex can be postulated as an intermediate. Furthermore, it is known[110] that ruthenium(III)-ammine complexes readily form chelated condensation products with carbonyl-containing organic species. Accordingly, $Ru(PhCOS)_2(PMe_2Ph)_2(NH_3)_2$ was prepared in chloroform solution, then treated with acetone to yield the desired complex both at room temperature and under reflux. Reaction of the diammine adduct with mesityl oxide (the Aldol condensation product of acetone) also yielded $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$ and on the basis of these various reactions, a mechanism is proposed for the formation of the imino-amino ligand (Scheme 2.3) which is analogous to the mechanism proposed by Evans *et al.*[110] for the condensation of carbonyl-containing species with $[Ru(NH_3)_6]^{3+}$ to form chelated organic ligands. Clearly, it is essential that the coordinated ammine groups are in *cis* positions, as has already been concluded from spectroscopic evidence for $Ru(PhCOS)_2(PMe_2Ph)_2(NH_3)_2$, and this provides an explanation for the failure to form the corresponding species starting from $RuCl_2(PPh_3)_3$ or $Ru(PhCOS)_2(PPh_3)_2(NH_3)_2$, where the ammine groups are in *trans* positions. The deprotonation of the ammonium ion to form ammonia which then reacts with $Ru(PhCOS)_2(PMe_2Ph)_2$ to give the diammine complex, is also important and is presumably carried out by the free dimethylphenylphosphine released when the starting complex reacted

with monothiobenzoate ion. This suggestion is supported by the fact that in the absence of base, $Ru(PhCOS)_2(PMe_2Ph)_2$ did not react with ammonium ion to give either the diammine complex or $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCh_2CMe_2NH_2)$.

Attempts were made to prepare analogous condensed chelates by altering the amine used, and by varying the ketonic solvent. However, although the diammine species $Ru(PhCOS)_2(PMe_2Ph)_2(NH_2Et)_2$ was readily formed, it showed no sign of undergoing condensation with either acetone or mesityl oxide, even though the spectroscopic studies discussed earlier confirm that this complex possesses the required cis-ammine stereochemistry. Attempts to condense $Ru(PhCOS)_2(PMe_2Ph)_2(NH_3)_2$ with methyl ethyl ketone were also unsuccessful, although when $[Ni(NH_3)_6][BF_4]_2$ was refluxed in methyl ethyl ketone for a few hours, a yellow crystalline product was formed which analysed for $[Ni(HNCEtCH_2CEtMeNH_2)_2][BF_4]_2$ and which exhibited characteristic bands in the i.r. spectrum between 3000 and 3300 cm^{-1} (N-H stretches), at 1660 cm^{-1} (coordinated imine C=N stretch) and at 1590 cm^{-1} ($-NH_2$ deformations), similar to those observed for $[Ni(HNCMeCH_2CMe_2NH_2)_2][BF_4]_2$[106]. This confirms that such a condensation is feasible for ketones other than acetone, and the failure of the reaction with $Ru(PhCOS)_2(PMe_2Ph)_2(NH_3)_2$ is probably best explained by simple steric factors inhibiting the formation of the bulkier 5-amino-3-imino-5-methylheptane ligand in an already fairly crowded coordination shell. Similarly, on substitution of ethylamine for ammonia, the condensed product, if formed, would be extremely sterically unfavourable. Attempts to extend the formation of condensed organic ligands in this system were not therefore pursued any further.

Efforts to isolate the 4-amino-2-imine-4-methylpentane molecule were also unsuccessful. For example, when $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$ was treated with carbon monoxide, the ligand was displaced and small amounts of $Ru(PhCOS)_2(PMe_2Ph)_2(CO)_2$,

with cis carbonyl groups as discussed earlier, were recovered. However, no identifiable organic product could be isolated. Attempts to protonate the ligand by treating the parent complex with HCℓ gas also led to its displacement, but again no organic product was recovered; presumably it is too unstable to exist as a free molecule[107].

2(iii) The Determination of the Crystal Structure of $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$

Crystals of the complex suitable for a single-crystal X-ray diffraction study were obtained from the reaction of mer-$RuCl_3(PMe_2Ph)_3$ with ammonium monothiobenzoate in acetone at room temperature, and no recrystallisation was attempted. The crystals were orange-brown in colour, and prismatic with fairly well-formed faces. A crystal of dimensions 0.3 × 0.3 × 0.4 mm was used, and preliminary oscillation and equi-inclination Weissenberg photographs, taken using CuK_α radiation, revealed that it was orthorhombic with cell dimensions:

$$a = 23.899(2)\text{Å}$$

$$b = 11.163(1)\text{Å}$$

$$c = 13.889(3)\text{Å}$$

(The cell dimensions were refined by the $\alpha_1 - \alpha_2$ splitting method using 23 zero-layer reflections with $\theta \geq 75^\circ$.) The diffraction pattern showed systematic absences as follows:

In the 0kℓ zone, $k + \ell = 2n + 1$ absent

In the hOℓ zone, $h = 2n + 1$ absent

In the hk0 zone, none absent.

There were no systematic absences due to centring, and on this basis

the space group was identified as $Pna2_1$ (N^o. 33), which is acentric with four equivalent positions or Pnam (alternative setting of Pnma, n^o 62) which is centred and has eight equivalent positions in the cell. Since a cell of the given dimensions containing eight molecules of any complex of ruthenium, dimethylphenylphosphine and monothiobenzoate groups would have a density of over 2g cm^{-2}, and the density of the crystals under investigation was measured by flotation as 1.34 g cm^{-2}, the acentric cell was chosen, on the assumption, from the spectroscopic evidence discussed earlier, that the molecule was not itself centrosymmetric, and the structure was solved in the space group $Pna2_1$. The calculated density, assuming four molecules of $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$ per unit cell, was 1.37 g cm^{-2}, which compares well with the measured value.

Data collection was carried out using an equi-inclination Weissenberg camera and CuK_α radiation, and photographs were taken up the b axis for k = 0-8, and up the c axis for ℓ = 0-6. The intensities were measured from the films by the S.R.C. Microdensitometer Service, and 2249 independent reflections were used to solve the structure, with a predicted R = 0.06, based on the internal consistency of the data. The X-Ray System computer programme package[111] was used and after data reduction, including the application of Lorentz and polarisation corrections, a Patterson map was calculated. Since ruthenium was by far the heaviest atom present, making up a substantial proportion of the total scattering matter in the crystal, the ruthenium-ruthenium spacings gave rise to the strongest peaks in the Patterson map and could easily be picked out, one per asymmetric unit. The four equivalent positions in the space group $Pna2_1$ are:

x y, z

$-x, -y, \frac{1}{2}+z$

$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$

$\frac{1}{2}+x, \frac{1}{2}-y, z$

and the Patterson map has Harker peaks at $(2x, 2y, \frac{1}{2})$ and at $(\frac{1}{2}-2x, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}-2y, 0)$. In the calculated Patterson map, peaks were observed on the Harker lines at (0.184, 0.5, 0.5) and at (0.5, 0.364, 0.0) giving values of 0.316 and 0.134 for 2x and 2y respectively. The observation of a peak at (0,3160, 0.1340, 0.5) in the Harker plane confirmed these values and accordingly the ruthenium atom was given the coordinates (0.158, 0.068, 0.500). The z coordinate is arbitrary in this space group, but must be fixed for one atom, and z = 0.5000 was chosen for convenience. A Fourier summation was then calculated using structure factors based on the observed intensities, with calculated phases based on the ruthenium position. However, the map thus produced exhibited mirror symmetry about the plane $(x, y, \frac{1}{2})$, which contained the ruthenium atom, and two independent sets of peaks identifiable as the sulphur and phosphorus atoms appeared in the map. One of these sets had to be correctly chosen by trial and error in order to break the pseudo-symmetry, and some difficulty was experienced in doing this. When a wrong set of peaks was picked, subsequent difference Fourier maps based on those peaks showed patterns of carbon atoms making up fragments of the expected ligands, but subsequent difference Fourier maps based on these showed no identifiable pattern and complete ligands making chemical sense were impossible to find. Once the correct set of four peaks, identified as two phosphorus and two sulphur atoms, had been chosen, however, all the non-hydrogen atoms were found without difficulty from a series of five difference Fourier maps. At this stage, with all the non-hydrogen atoms included,

R = 0.152 and a different Fourier map showed no significant peaks. The atomic positions and temperature factors (anisotropic for Ru, P and S atoms and isotropic for C, N and O atoms) were then refined, using the block-diagonal least squares method, and in the final cycles a weighting scheme was applied to reduce the contribution from reflections of low $\sin\theta$ value or large F_{obs} (specifically, a weighting factor W was applied, such that $W = XY$ where $X = (\sin\theta)/0.3$ for $\sin\theta < 0.3$, otherwise $X = 1.0$, and $Y = 35/|F_{obs}|$ for $|F_{obs}| > 35$, otherwise $Y = 1.0$). No extinction corrections were applied* and on the last cycle the refinement converged, with no atomic parameter shifting by more than 0.5 times the standard deviation. The final (unweighted) R = 0.067, which compares reasonably well with the value of 0.06 predicted for the data set. A final examination of the data, sorted in terms of $\sin\theta/\lambda$ and F_{obs}, showed that errors were randomly distributed. Final values of fractional coordinates and thermal parameters are given in Table 2.4 and a structure factor table is given in Table 2.7.

2(iv) Discussion of the Structure

The interatomic distances and angles for the complex are given in Tables 2.5 and 2.6, and the molecular structure and crystal packing are shown in Figures 2.1 and 2.2.

The coordination about the ruthenium is in the form of a distorted

---

* Primary extinction is unimportant for non-perfect crystals, and a graph of $(F_{calc})^2/(F_{obs})^2$, which has a slope of 2g, where g = secondary extinction coefficient, showed that secondary extinction was negligible[112].

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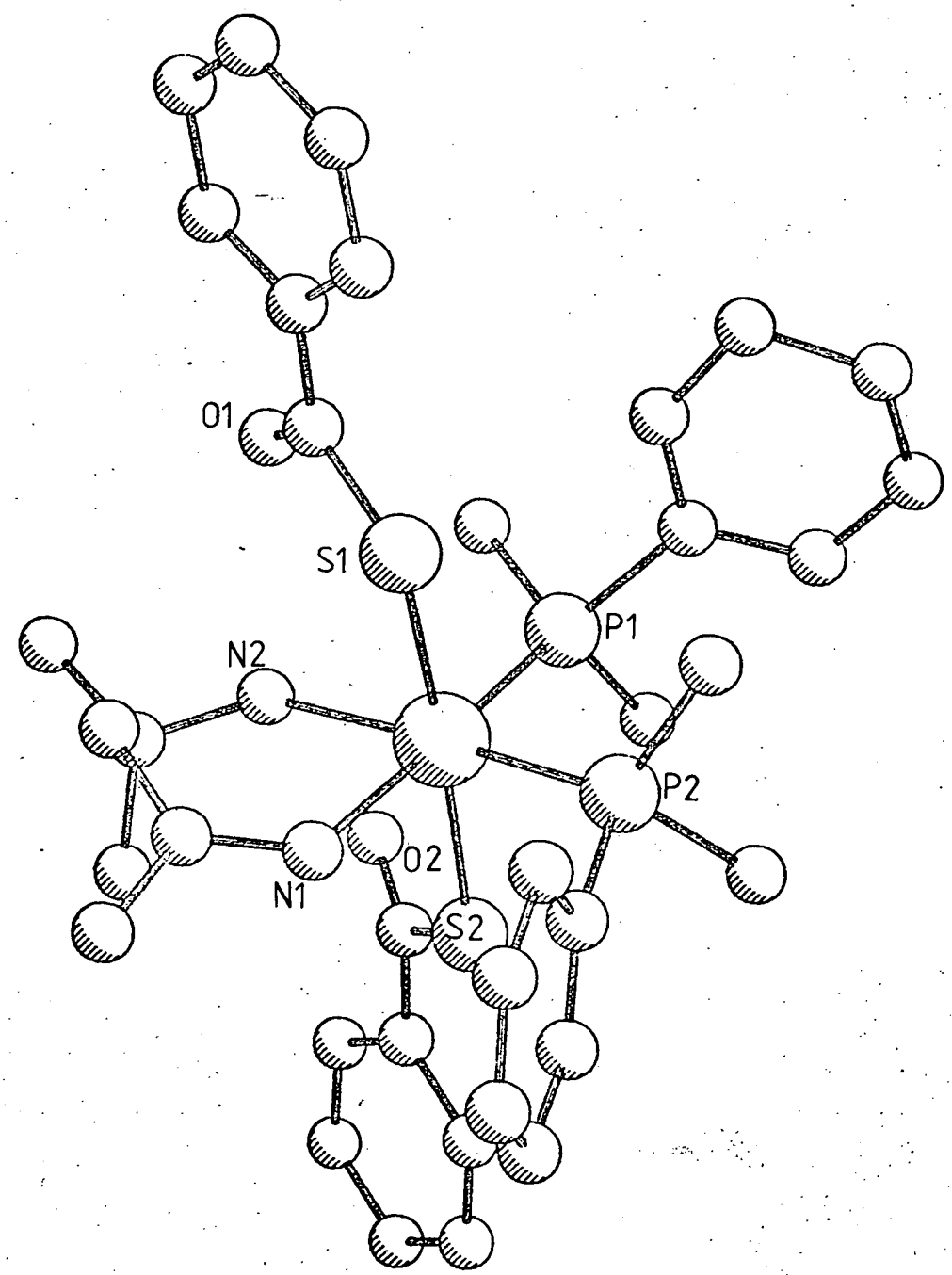


Figure 2.1 Molecular structure of $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$

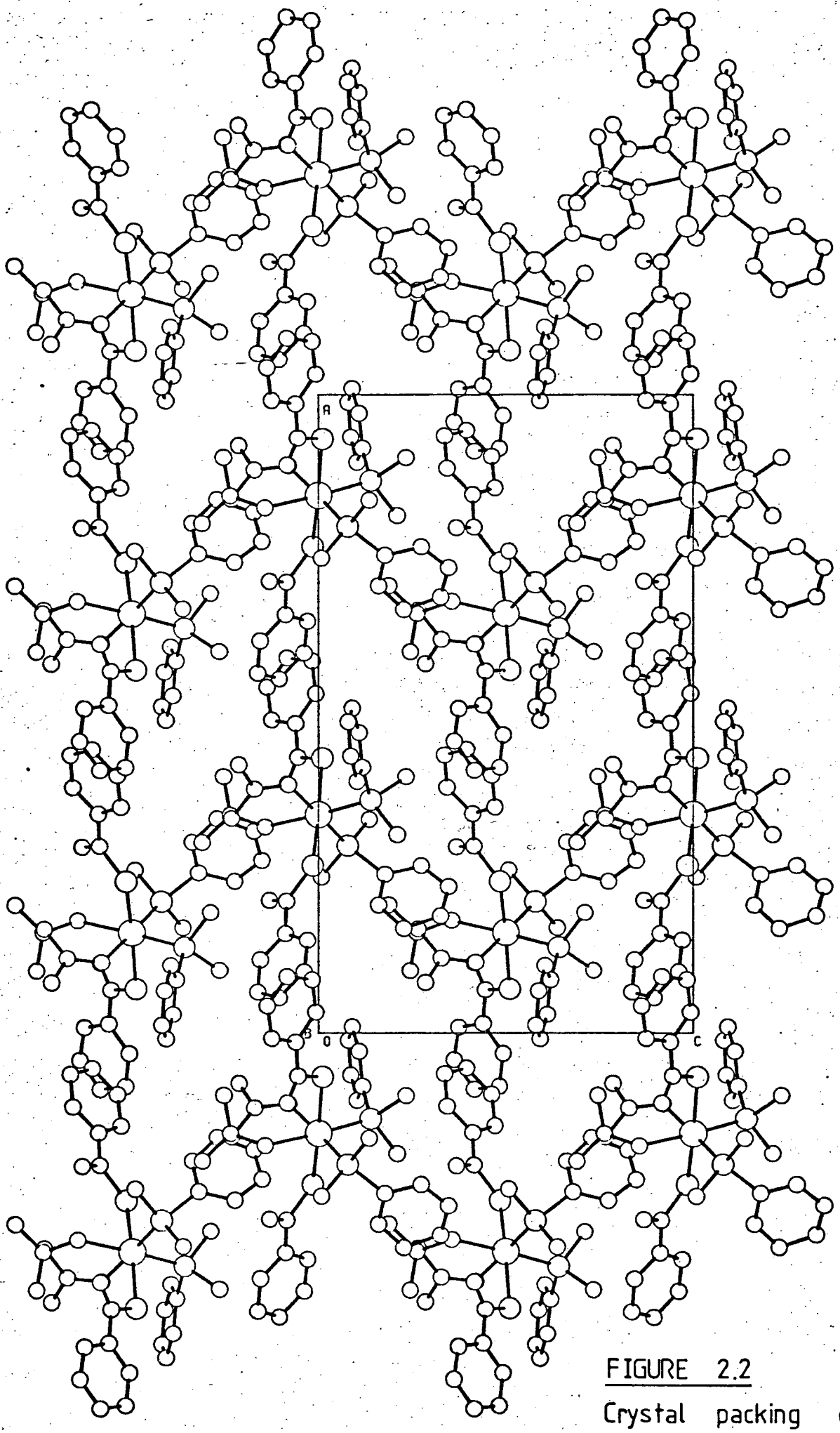


FIGURE 2.2

Crystal packing of $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2$

octahedron, with Ru-P and Ru-S distances fairly typical for this type of complex, and with cis-phosphines and trans-sulphurs as predicted from the spectroscopic evidence. This tends to confirm the cis-phosphine stereochemistry assigned earlier for $Ru(PhCOS)_2(PMe_2Ph)_2(NH_3)_2$ and the other $Ru(PhCOS)_2(PMe_2Ph)_2L_2$ complexes. The uncoordinated oxygens of the monothiobenzoate ligands are both within good hydrogen-bonding distances (2.870Å and 2.851Å) of the coordinated amine nitrogen, although to achieve this, one monothiobenzoate is twisted such that the ruthenium is no longer coplanar with the acid group (Ru - S1 - C9 - O1 = 14°). This hydrogen bonding presumably lends stability to the structure, and accounts for the lowering of the $\nu_{(CO)}$ stretching frequency in the i.r. spectrum, discussed above. The geometry and coordination of the imino-amine ligand are in agreement with the results published for trans-$[Cu(HNCMeCH_2CMe_2NH_2)_2]^{2+}$ [109], with the Ru-N(imine) bond some 0.12Å shorter than the Ru-N(amine) bond, and C-N(imine) a significant 0.15Å shorter than C-N(amine). The chelate ring is almost free from steric strain, with no ring angle significantly different from the expected values for tetrahedral and trigonal carbon, and the Ru-N-C ring angles of 128.2° and 122.7° for the imine and amine nitrogens respectively exhibiting the only major deviations from ideal dimensions. In the monothiobenzoate ligand, the C-S distances (1.81Å and 1.74Å) and C-O distances (1.20Å and 1.29Å) are not greatly different from those found in previous structural studies of monothiobenzoate complexes[9,30], although in previous cases the acid ligands have been bidentate and comparisons are further hampered by the discrepancy in the dimensions found for the two monothiobenzoate ligands in the present case. Both the dimethylphenylphosphine groups

are twisted so as to minimise the steric interactions between the phosphine phenyl rings and the neighbouring end of the imino-amino ligand, and the presence of side-chains on the coordinated nitrogens would clearly increase the strain in the system to an unacceptable level. This may account for the failure of condensation reaction using $Ru(PhCOS)_2(PMe_2Ph)_2(NH_2Et)_2$ and similar steric problems inhibit the condensation of $Ru(PhCOS)_2(PMe_2Ph)_2(NH_3)_2$ with methyl ethyl ketone, which would give a chelate ring with ethyl groups on the α-carbon atoms.

EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzil. Infrared spectra were recorded in the range 250-4000 cm^{-1} region on a Perkin-Elmer 557 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Hydrogen-1 nmr spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable temperature probe, and proton noise-decoupled ^{31}P nmr spectra on a Varian XL 100 spectrometer operating in the pulse and Fourier-transform modes at 40.5MHz (^{31}P chemical shifts quoted in p.p.m. to high frequency of 85% H_3PO_4). Mass spectra were obtained on an AEI MS9 spectrometer. Melting points were determined with a Kofler hot-stage microscope and are uncorrected. Crystallographic calculations were made using the "X-Ray-72" system[111] as implemented at the Edinburgh Regional Computing Centre. Ruthenium(III) trichloride trihydrate (Johnson Matthey Ltd.), carbon monoxide (Air Products), triphenylphosphine (B.D.H.), dimethylphenylphosphine (Maybridge Chemical Company)

and monothiobenzoic acid (Aldrich) were obtained as indicated. $NH_4[PhCOS]$ and $Na[PhCOS]$ were prepared by reaction of PhCOSH with ammonia gas in benzene and Na_2CO_3 in water respectively. $RuCl_2(PPh_3)_3$[105], mer-$RuCl_3(PMe_2Ph)_3$[116] and all trans-$RuCl_2(CO)_2(PPh_3)_2$[105], were prepared as described earlier. All the solutions were degassed before use and reactions were carried out under a nitrogen atmosphere.

Bis(monothiobenzoato)bis(triphenylphosphine)ruthenium(II):- The compounds $RuCl_2(PPh_3)_3$ (0.20g) and $Na[PhCOS]$ (0.40g) were refluxed in degassed acetone (50 ml) for 3h. The resulting orange-yellow product was filtered off and washed with acetone and diethyl ether (0.15g, 88%) m.p. 218 - 220°C (Found: C, 65.7; H, 4.7. Calc. for $C_{50}H_{40}O_2P_2RuS_2$: C, 66.7; H, 4.4%).

The same product can also be obtained by reaction of $NH_4[PhCOS]$ with $RuCl_2(PPh_3)_3$.

Bis(ammine)bis(monothiobenzoato)bis(triphenylphosphine)ruthenium(II):- Ethanol (20 ml) was saturated with ammonia gas and then $Ru(PhCOS)_2(PPh_3)_2$ (0.10g) was added. The suspension was stirred at room temperature for 3h and the resulting bright yellow product was filtered off and washed with acetone and diethyl ether (0.09g, 86%) m.p. 205 - 208°C (Found: C, 64.5; H, 5.0; N, 2.7 Calc. for $C_{50}H_{46}N_2O_2P_2RuS_2$: C, 64.4; H, 4.9; N, 3.0%).

Di(carbonyl)bis(monothiobenzoato)bis(triphenylphosphine)ruthenium(II):- Method a) The compound $Ru(PhCOS)_2(PPh_3)_2$ (0.10g) was suspended in ethanol (50ml) and refluxed under carbon monoxide gas for 3h. The bright lemon yellow product was separated from unreacted starting material by dissolving it in dichloromethane, filtering and recrystallising the product m.p. 235 - 239°C (Found: C, 65.2; H, 4.7 Calc. for $C_{52}H_{40}O_4P_2RuS_2$: C, 65.3; H, 4.2%).

Method b) The compounds all trans- $RuCl_2(CO)_2(PPh_3)_2$ (0.05g) and $NH_4[PhCOS]$ (0.05g) were refluxed in acetone (50ml) for 2h. The resulting bright yellow solution was filtered hot, then the volume was reduced and petroleum ether (bp 40-60°C) was added. The lemon yellow product was then filtered off.

Bis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II):-
The compounds mer- $RuCl_3(PMe_2Ph)_3$ (0.20g) and $Na[PhCOS]$ (0.20g) were refluxed in acetone (50ml) for 3h. The solution was filtered hot, then the volume was reduced and water was added to yield a red-brown precipitate which was filtered off and dried under vacuo over calcium chloride (0.17g, 70%) m.p. 169 - 171°C (Found: C, 55.5, H, 5.0 M($CHCl_3$) 636. Calc. for $C_{30}H_{32}O_2P_2RuS_2$: C, 55.3, H, 4.9% M 651). The compound can also be prepared as above using $Na[PhCOS]$ or $NH_4[PhCOS]$ in methanol as solvent.

Bis(ammine)bis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II):-
The compound $Ru(PhCOS)_2(PMe_2Ph)_2$ (0.20g) was dissolved in chloroform (10ml) and ammonia gas was bubbled through the solution at room temperature for 10m to give a yellow-brown solution. The product was not isolated but was identified by ^1H and ^{31}P nmr studies using a sample prepared in $CDCl_3$ (see discussion section). Attempts at isolation were however unsuccessful. When the volume of the solution was reduced, yellow-brown products resulted which analysed for mono- and bis-hydrated species containing only one coordinated ammine group. The ^1H n.m.r. spectra were not similar to those obtained from samples prepared in situ, and no further attempts at characterisation were made.

Di(carbonyl)bis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II):
The compound $Ru(PhCOS)_2(PMe_2Ph)_2$ (0.10g) was dissolved in ethanol (30ml) and then carbon monoxide gas was bubbled through the solution at

room temperature for 1h to give a pale yellow solution. The volume of the solution was reduced and it was cooled over ice to yield a pale cream crystalline powder which was filtered off and dried under vacuo (0.06g, 51%) m.p. 153 - 155°C (Found: C, 53.8; H, 4.6 Calc. for $C_{32}H_{32}O_4P_2RuS_2$: C, 54.2; H, 4.5%).

Bis(dimethylphenylphosphine)bis(ethylamine)bis(monothiobenzoato)ruthenium(II): The compound $Ru(PhCOS)_2(PMe_2Ph)_2$ (0.10g) was refluxed in chloroform (20ml) with ethylamine (0.50ml; 70% aqueous solution) for 1h. Ethanol (10ml) was then added and the chloroform was evaporated off to yield a yellow-brown crystalline powder which was filtered off and washed with cold ethanol (0.10g, 93%) m.p. 177 - 180°C (Found: C, 54.0; H, 6.0; N, 3.7 Calc. for $C_{34}H_{46}N_2O_2P_2RuS_2$: C, 55.1; H, 6.2; N, 3.8%).

(4-Amino-2-imino-4-methylpentane)bis(dimethylphenylphosphine)bis-(monothiobenzoato)ruthenium(II) Method a) The compounds mer- $RuCl_3(PMe_2Ph)_3$ (0.30g) and $NH_4[PhCOS]$ (0.30g) were dissolved in the minimum volume of acetone (20ml), the solution was filtered and left to stand at room temperature under nitrogen for 72h, after which time clear orange-brown crystals were removed from the flask. The complex was also prepared by refluxing the above reaction mixture in acetone (50ml) for 2h, reducing the volume of the solution and then cooling it in ice to yield a yellow powder which was filtered off and recrystallised from chloroform (0.26g, 72%) m.p. 208 - 210°C (Found: C, 54.4; H, 5.6; N, 3.3 M, ($CHCl_3$) 724. Calc for $C_{36}H_{46}N_2O_2P_2RuS_2$: C, 56.5; H, 6.0; N, 3.7% M, 765). Method b) The compound $Ru(PhCOS)_2(PMe_2Ph)_2$ (0.10g) in chloroform (10ml) was treated with ammonia gas to give the bisammine complex in situ (see earlier). Acetone (30ml) was then added and the solution was left to stand for 3h at room temperature when the complex was obtained as a yellow powder as in method a). Similarly,

$Ru(PhCOS)_2(PMe_2Ph)_2$ (0.10g) in chloroform (10 ml) treated with ammonia gas and then with mesityl oxide (5ml) yielded the complex after standing at room temperature. The complex was also obtained in both cases when the solutions were refluxed.

Bis-(5-amino-3-imino-5-methylheptano)nickel(II) tetrafluoroborate:-

The salt $[Ni(NH_3)_6][BF_4]_2$ (0.1g) was refluxed in methylethylketone (50 ml) for 4h. The volume of the resulting yellow solution was reduced and diethyl ether was added to yield a yellow crystalline product (0.11g, 70%) m.p. > 260°C, decomp. (Found: C, 36.44; H, 6.50; N, 10.67. Calc. for $B_2C_{16}F_8H_{36}N_4Ni$: C, 37.70; H, 6.96; N, 10.83%.)

TABLE 2.1

Mull infrared spectra of various monothiobenzoate complexes of ruthenium(II)

Complex	PhCOS vibrations (cm^{-1})		Other useful bands (cm^{-1})
	ν_{CO}	ν_{CS}	
Na[PhCOS]	1500	960	
$Ru(PhCOS)_2(PPh_3)_2$	1500	965	
$Ru(NH_3)_2(PhCOS)_2(PPh_3)_2$	1550	935	
$Ru(CO)_2(PhCOS)_2(PPh_3)_2$	1590, 1570	935	1950 (ν_{CO})
$Ru(PMe_2Ph)_2(PhCOS)_2$	1470	965	
$Ru(CO)_2(PMe_2Ph)_2(PhCOS)_2$	1600, 1570	945	2025, 2005 (ν_{CO})
$Ru(PMe_2Ph)_2(EtNH_2)_2(PhCOS)_2$	1525	935	
$Ru(PMe_2Ph)_2(PhCOS)_2(HNC(Me)CH_2CMe_2NH_2)$	1530	935	3350, 3000 (ν_{NH_2}) 1660 ν_{CN}(imine) 1585 (δ_{NH_2})

TABLE 2.2

^{1}H n.m.r. data in $CDC\ell_3$ for some ruthenium(II) monothiobenzoate complexes

Complex	T/K	δ ± 0.01 ppm[a] Methyl of Phosphine	Other ligand resonances
$Ru(PMe_2Ph)_2(PhCOS)_2$	300	1.42(pt); 1.57(t)	7.00-8.00(m)[b]
	260	1.32(pt), 1.46(pt) 1.57(t)	
$Ru(NH_3)_2(PMe_2Ph)_2(PhCOS)_2$	300	1.75(pt)	7.00-8.00(m)[b]
$Ru(CO)_2(PMe_2Ph)_2(PhCOS)_2$	300	1.60(pt)	7.00-8.00(m)[b]
	260	1.60(pt)	
$Ru(PMe_2Ph)_2(EtNH_2)_2(PhCOS)_2$	300	1.74(pt)	7.00-8.30(m)[b]
$Ru(PMe_2Ph)_2(PhCOS)_2(HNC(Me)-CH_2CMe_2NH_2)$	300	1.43(d), 1.86(d)	7.00-8.00(m)[b]
	250	1.03(d), 1.20(d) 1.95(t)[c]	1.06(s)[d], 1.58(s)[d] 2.31(s)[d] 5.80(broad)[e]

[a] S = singlet, d = doublet, t = triplet, pt = pseudotriplet, m = multiplet

[b] Phenyl resonances [c] overlapping doublet of doublets [d] gem-methyls, imine-C-methyl and methylene protons from $HNC(Me)CH_2CMe_2NH_2$ ligand.

[e] NH_2 protons.

TABLE 2.3

$^{31}P-\{^{1}H\}$-n.m.r. data in $CDC\ell_3$ for some ruthenium(II) monothiobenzoate complexes

Complex	δ ± 0.01 p.p.m.	J(PP)
$Ru(PhCOS)_2(PPh_3)_2$	59.87 (s)	
$Ru(PhCOS)_2(PPh_3)_2(NH_3)_2$	46.30 (s)	
$Ru(PhCOS)_2(PPh_3)_2(CO)_2$	42.83 (s)	
$Ru(PhCOS)_2(PMe_2Ph)_2$	39.00 (s)	
	4.57 (m)	
$Ru(PhCOS)_2(PMe_2Ph)_2(NH_3)_2$	23.66 (s)	
$Ru(PhCOS)_2(PMe_2Ph)_2(CO)_2$	-10.79 (s)	
$Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2\backslash Me_2NH_2)$	16.77 (d)	33
	23.04 (d)	33

s = singlet d = doublet m = multiplet

TABLE 2.4

Atomic Positional and Thermal Parameters (all $\times 10^4$) for (1)

with Estimated Standard Deviations in brackets

Atom	x/a	y/b	z/c	U.
Ru	1574.6(4)	695.3(10)	5000	*
P1	2062(2)	-793(4)	5786(4)	*
P2	1345(2)	1660(4)	6406(4)	*
S1	691(2)	-318(4)	5106(5)	*
S2	2375(2)	1985(4)	4842(4)	*
O1	1098(5)	-2174(11)	4162(9)	446(32)
O2	2919(6)	474(13)	3680(12)	657(41)
N1	1108(6)	2007(13)	4197(12)	418(38)
N2	1767(6)	-174(13)	3560(11)	380(36)
C1	2512(7)	-335(15)	6783(14)	390(44)
C2	1651(9)	-2000(20)	6363(18)	641(61)
C3	2556(8)	-1702(17)	5079(22)	627(53)
C4	2992(9)	324(21)	6614(19)	535(64)
C5	2378(9)	-576(20)	7745(17)	639(59)
C6	3163(10)	615(24)	8262(19)	774(71)
C7	3360(10)	846(22)	728(18)	734(67)
C8	2705(9)	-100(22)	8476(19)	717(69)
C9	676(7)	-1716(16)	4448(13)	369(42)
C10	143(7)	-2290(16)	4388(13)	356(42)
C11	-323(6)	-2044(14)	4928(20)	459(41)
C12	-835(7)	-2650(17)	4829(17)	560(55)
C13	-883(8)	-3573(19)	4159(16)	524(52)
C14	423(9)	-3814(20)	3617(17)	592(58)

TABLE 2.4 (Contd.)

Atom	x/a	y/b	z/c	U.
C15	88(7)	-3219(18)	3741(16)	467(48)
C16	2931(7)	1474(17)	4146(14)	414(44)
C17	3439(7)	2148(16)	4118(14)	415(41)
C18	3544(8)	3161(19)	4706(16)	630(63)
C19	4039(10)	3799(21)	4616(18)	722(71)
C20	4447(10)	3458(22)	3951(19)	712(68)
C21	4358(9)	2497(21)	3365(18)	647(62)
C22	3850(8)	1822(18)	3432(16)	530(53)
C23	1890(8)	2420(18)	7105(15)	483(50)
C24	834(8)	2876(17)	6187(15)	460(48)
C25	290(8)	2699(18)	6096(16)	510(52)
C26	-94(10)	3653(22)	5910(19)	704(68)
C27	120(10)	4779(22)	5799(19)	692(68)
C28	660(11)	4996(24)	5869(21)	789(76)
C29	1058(10)	4101(23)	6039(20)	785(76)
C30	982(8)	804(20)	7341(16)	563(54)
C31	1578(9)	338(18)	2630(16)	564(53)
C32	1174(8)	2331(17)	3280(15)	476(49)
C33	792(9)	3302(19)	2858(18)	590(56)
C34	2009(10)	187(22)	1879(20)	722(71)
C35	1632(8)	1770(18)	2661(15)	507(50)
C36	977(9)	-50(21)	2454(18)	638(62)

* Anisotropic thermal parameters ($\times 10^4$)

(1) = $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMe_2CH_2CMe_2NH_2)$

TABLE 2.4 (Contd.)

Atom	U11	U22	U33	U12	U13	U23
Ru	274(3)	313(4)	381(5)	2(5)	10(9)	16(10)
P1	304(21)	362(25)	469(28)	53(21)	-30(21)	59(27)
P2	320(21)	320(23)	383(28)	24(20)	23(21)	-17(23)
S1	272(16)	363(20)	473(32)	-17(14)	46(27)	-76(28)
S2	341(18)	372(20)	388(34)	-36(16)	20(23)	22(25)

TABLE 2.5

Bond lengths in (1) in Angstroms with Estimated Standard Deviations in brackets

Ru-P1	2.305(5)
Ru-P2	2.295(5)
Ru-S1	2.400(4)
Ru-S2	2.405(4)
Ru-N1	2.151(15)
Ru-N2	2.271(15)
P1-C1	1.825(19)
P1-C2	1.850(23)
P1-C3	1.839(23)
P2-C23	1.832(20)
P2-C24	1.852(19)
P2-C30	1.831(22)
S1-C9	1.807(19)
C9-O1	1.198(20)
C9-C10	1.428(23)
S2-C16	1.739(19)
C16-O2	1.291(24)
C16-C17	1.430(25)
phenyl C-C (average)	1.39(4)
N1-C32	1.333(26)
C32-C33	1.53(3)
C32-C35	1.53(3)
C35-C31	1.60(3)
C31-C34	1.54(3)
C31-C36	1.52(3)
C31-N2	1.482(26)
N2-O1	2.870(19)
N2-O2	2.851(19)

TABLE 2.6

Bond angles in (1) in Degrees, with Estimated Standard Deviations in brackets

P1-Ru-P2	93.19(17)
P1-Ru-S1	94.37(16)
P1-Ru-S2	94.14(16)
P1-Ru-N1	176.48(43)
P1-Ru-N2	90.40(39)
P2-Ru-S1	87.66(19)
P2-Ru-S2	89.22(17)
P2-Ru-N1	89.90(43)
P2-Ru-N2	176.39(40)
S1-Ru-S2	171.08(15)
S1-Ru-N1	84.08(39)
S1-Ru-N2	91.74(38)
S2-Ru-N1	87.57(39)
S2-Ru-N2	90.84(38)
N1-Ru-N2	86.50(55)
Ru-P1-C1	117.1(6)
Ru-P1-C2	117.4(7)
Ru-P1-C3	117.9(9)
C1-P1-C2	100.9(10)
C1-P1-C3	100.5(10)
C2-P1-C3	99.9(10)
P1-C1-C4	120.5(16)
P1-C1-C5	122.3(14)
Ru-P2-C23	119.9(6)
Ru-P2-C24	111.2(7)
Ru-P2-C30	118.1(7)
C23-P2-C24	102.4(9)
C23-P2-C30	101.7(1.0)
C24-P2-C30	100.7(9)
P2-C24-C25	123.7(1.5)
P2-C24-C29	117.4(1.5)
Ru-S1-C9	113.2(6)
Ru-S2-C16	117.5(6)

TABLE 2.6 (Contd.)

O1-C9-S1	121.3(1.3)
O1-C9-C10	122.6(1.6)
S1-C9-C10	115.8(1.2)
C9-C10-C11	127.1(1.7)
C9-C10-C15	117.5(1.6)
O2-C16-S2	123.1(1.4)
O2-C16-C17	117.4(1.6)
S2-C16-C17	119.4(1.4)
C16-C17-C18	123.7(1.7)
C16-C17-C22	118.2(1.7)
phenyl C-C-C (average)	119.8(2.0)
Ru-N1-C32	128.2(1.2)
Ru-N2-C31	122.7(1.1)
N1-C32-C35	120.8(1.7)
N1-C32-C33	119.0(1.7)
C33-C32-C35	120.2(1.8)
C32-C35-C31	111.5(1.6)
C35-C31-N2	109.7(1.6)
C35-C31-C34	105.7(1.7)
C35-C31-C36	111.4(1.7)
N2-C31-C34	105.5(1.7)
N2-C31-C36	108.5(1.7)
C34-C31-C36	115.8(1.9)

Table 2.7: Structure factors for $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$

Columns are h, $10|F_o|$, $10|F_c|$, and phase (degrees).

H,0,0

6	285	293	0
8	251	198	180
10	588	698	180
12	1085	1265	0
14	528	551	0
16	595	618	180
18	229	225	0
20	479	475	0
22	1055	1019	180
24	252	265	0
26	329	306	0
28	228	228	180

H,1,0

4	38	115	180
5	815	861	180
6	615	752	0
7	546	705	0
8	175	285	180
9	1189	1371	180
10	218	219	180
11	218	309	180
12	319	379	0
13	1003	1059	0
14	690	707	180
15	339	353	180
16	314	335	0
17	272	304	180
19	568	585	0
20	656	611	0
21	339	321	180
23	609	533	180
24	296	259	0
25	365	358	0
26	250	189	180

H,2,0

0	375	362	0
1	930	1095	180
3	896	567	0
4	195	133	0
6	659	819	0
7	727	766	180
8	1191	1289	180
9	1165	1303	180
10	295	270	180
11	427	534	0
12	876	986	0
13	207	260	180
14	516	585	0
15	393	432	180
16	891	891	180
17	512	517	0
18	303	316	0
20	372	355	0
21	392	285	180
22	583	564	180
24	210	105	0
27	424	383	180
29	162	193	0

H,3,0

1	238	178	0
2	493	570	180
3	208	282	0
6	1849	1897	0
7	333	278	180
8	1636	1958	180
9	538	570	180
10	816	895	0
11	809	849	0
12	602	590	0
13	389	370	0
14	957	1029	180
16	194	176	0
17	262	297	180
18	701	697	0
19	172	162	0
20	546	582	180
21	305	320	180
22	249	213	180
24	267	222	0
28	313	369	180
29	188	139	180

H,4,0

1	382	279	180
3	609	698	180
4	359	383	0
5	1386	1501	0
6	394	414	180
7	1035	1161	180
8	245	269	180
11	1108	1156	0
12	249	240	0
13	537	532	180
14	186	165	180
15	718	749	180
16	340	316	0
17	807	915	0
20	298	283	180
21	448	419	180
23	247	238	0
24	239	219	180
27	470	465	180

H,5,0

1	293	226	0
2	295	294	180
3	260	316	0
5	350	368	180
6	528	556	0
8	987	1026	180
9	305	269	0
10	259	280	0
11	229	190	180
13	372	409	180
14	791	824	180
16	354	348	0
17	697	636	0
18	562	573	0
19	620	592	180
20	368	365	180
24	335	342	0
25	247	256	180
26	188	182	180

H,6,0

0	297	280	180
1	636	620	180
2	868	831	0
3	209	222	0
4	459	448	0
5	658	676	0
6	903	925	180
7	218	188	180
8	381	365	0
9	417	463	180
11	157	192	0
12	235	287	180
13	170	188	180
16	837	873	0
17	553	591	0
18	381	332	180
19	237	242	0
20	800	819	180
21	218	198	180
22	574	515	0
26	299	300	180

H,7,0

1	607	634	180
3	775	812	0
4	376	335	0
5	509	546	180
6	332	369	0
7	373	352	180
8	235	216	180
10	380	401	180
11	273	208	0
12	177	167	0
13	583	616	180
14	282	266	180
15	527	515	0
19	618	606	180
23	461	445	0
25	498	473	180

H,8,0

0	1208	1219	180
1	192	211	0
2	755	747	0
3	107	126	0
4	820	868	0

6	588	581	180
8	277	261	180
10	742	745	0
11	863	874	180
12	819	828	180
13	302	310	0
14	199	220	180
16	862	866	0
18	153	182	180
19	206	191	0
20	331	290	180
22	869	881	0
28	157	116	180

H,9,0

1	802	786	180
2	514	516	0
3	488	502	0
7	808	851	180
8	229	268	0
9	625	639	0
10	266	278	180
11	350	358	0
12	803	833	180
13	540	563	180
14	825	849	0
17	263	250	0
19	195	186	180

H,10,0

1	552	567	0
3	502	509	0
5	452	447	180
6	246	230	180
7	220	208	0
9	392	392	0
11	612	597	180
13	272	279	0
14	322	281	180
15	273	261	0

H,11,0

2	596	639	0
3	251	272	180
4	250	268	180
5	181	178	0
6	868	868	180
8	568	580	0
10	386	391	180
12	249	256	180
14	285	261	0
17	208	209	180
18	208	198	180

H,12,0

4	257	285	180
6	388	388	0
7	308	306	0
11	352	388	180
15	170	173	0

H,13,0

3	382	358	180
5	168	156	0
7	288	308	0
10	158	177	180

H,0,1

4	1073	1247	51
6	886	880	55
8	730	922	255
10	561	515	48
12	962	989	111
14	990	1037	287
16	442	394	11
18	281	206	206
20	759	757	255
22	294	251	257
24	722	717	42
26	211	199	271

H,1,1

3	706	702	177
4	920	1023	80
5	890	1085	72

7	738	862	289
8	578	696	289
9	351	385	327
12	208	224	258
13	246	195	121
15	695	712	269
16	286	306	73
17	458	459	57
18	315	320	203
20	211	200	253
21	748	702	268
22	362	347	14
23	711	615	89
26	310	211	247
27	266	217	257
28	273	228	88

H,2,1

1	686	681	227
2	1372	1476	237
3	1193	1207	95
4	860	811	18
5	828	816	148
6	321	303	220
7	1146	1146	271
8	977	1111	286
9	765	857	71
10	1182	1261	70
11	428	508	116
12	818	803	86
13	868	921	268
14	828	880	272
15	796	863	172
16	300	290	266
18	528	491	89
19	278	278	220
20	639	635	292
21	297	303	276
23	241	215	70
24	377	358	101
25	353	324	285
29	338	312	88

H,3,1

0	1026	913	281
1	626	573	89
2	863	882	358
3	669	599	226
4	1348	1315	127
5	846	555	35
6	1458	1535	276
7	1092	1057	286
8	319	325	268
9	478	449	89
10	523	509	100
11	355	405	87
12	809	888	281
13	200	227	26
14	215	212	196
15	395	389	241
16	870	922	89
17	309	291	137
18	528	498	296
20	837	886	261
21	233	193	310
22	353	345	76
23	276	261	132
25	288	290	133
26	381	382	277
28	382	388	93

H,4,1

1	397	373	280
2	688	661	210
3	757	880	56
4	756	815	285
6	867	839	306
7	1299	1406	268
8	455	430	80
9	1235	1360	92
10	363	368	186
11	313	363	311
12	183	220	225
13	507	514	277
15	901	888	109
17	825	833	78
18	833	833	288
19	774	744	276
21	320	301	88
23	236	228	87

25	118	315	270

H,5,1

0	388	407	285
1	561	512	190
2	460	461	78
3	260	272	182
4	803	379	106
5	579	585	288
6	905	925	281
7	1059	1123	90
8	811	841	187
9	329	320	17
10	739	705	65
12	608	653	288
13	284	261	218
14	323	311	156
15	652	670	91
16	733	757	97
17	891	866	291
18	325	336	292
19	259	251	258
20	340	337	268
21	292	305	122
22	328	298	90
23	266	272	290
26	303	320	282
27	177	218	98

H,6,1

1	363	377	89
2	725	731	101
3	605	650	80
4	942	1000	275
5	284	301	258
6	508	583	188
7	599	617	269
8	695	689	59
10	226	247	338
11	288	285	96
13	391	406	258
14	518	496	112
15	828	830	90
18	886	881	279
20	530	512	98
21	212	233	282
24	394	396	285
25	275	269	258
26	266	258	95

H,7,1

0	299	281	223
1	1175	1171	97
2	869	876	78
3	289	279	311
5	671	721	268
6	308	276	297
7	808	776	118
8	198	818	276
9	868	869	86
11	592	602	271
12	311	338	129
13	251	201	109
14	237	208	2
15	851	856	93
16	219	216	50
17	612	628	277
20	186	188	255
21	668	681	96
22	218	178	111
23	168	319	277

H,8,1

1	178	178	81
2	880	929	96
3	258	269	283
4	603	583	288
6	179	177	113
7	186	207	253
8	158	181	66
9	363	359	286
10	298	307	226
11	152	157	165
12	870	876	270
13	837	844	101
14	550	561	86
17	210	211	105
18	356	359	278

H,0,2

2	628	696	325
4	290	309	107
6	717	579	70
8	210	139	35
10	1075	1215	181
12	845	927	348
14	782	840	33
16	679	688	175
18	682	610	297
20	338	311	9
22	877	863	179
26	884	878	332
28	214	208	176

H,1,2

1	1194	1087	353
2	1070	1038	278
3	1460	1588	211
4	881	882	310
5	631	650	60
6	161	182	117
7	518	571	299
8	345	390	219
9	1215	1331	169
10	304	268	283
11	883	890	232
12	372	455	9
13	898	1021	353
14	657	735	169
15	178	300	118
16	558	556	312

17	457	461	240
19	563	538	7
21	888	831	186
23	579	585	168
24	810	372	337
25	880	886	9
26	266	227	155

H,2,2

0	1257	1156	108
1	526	525	123
2	985	819	52
3	1303	1198	305
4	1119	1105	185
5	548	516	356
6	1257	1206	329
7	815	845	175
8	968	973	163
9	997	1029	206
10	559	619	148
11	812	814	27
12	193	241	345
13	375	383	164
14	738	757	7
15	318	346	168
16	317	261	183
17	610	564	341
18	409	402	14
20	293	253	83
21	450	440	131
22	698	646	219
23	369	352	308
26	286	223	18
27	451	416	175

H,3,2

1	466	386	235
2	1045	1003	165
3	556	581	131
4	1747	1628	8
5	258	216	334
6	985	952	38
7	719	675	297
8	1602	1658	176
9	626	695	159
10	411	472	5
12	305	318	357
13	273	278	351
14	725	750	183
15	367	370	321
16	398	408	59
17	230	190	153
18	588	590	345
19	329	265	35
20	517	501	168
21	330	309	193
23	241	224	270
24	316	318	348
26	249	221	165
28	333	382	188

H,4,2

0	283	301	210
1	706	690	150
2	851	838	28
3	159	229	169
4	842	888	75
5	1555	1559	2
6	399	427	220
7	535	585	182
8	576	516	278
9	708	837	190
11	886	936	14
13	594	622	283
15	521	508	154
17	683	683	24
20	295	301	168
21	885	838	176
27	829	817	208

H,5,2

1	370	338	242
2	850	868	169
3	1053	1035	355
4	800	778	195
5	474	434	198
6	176	206	319
7	844	817	187
8	899	883	186

9	699	717	356
10	397	398	48
11	261	258	208
12	463	513	321
13	328	320	118
14	826	778	209
16	251	255	65
17	491	488	8
18	531	518	357
19	626	620	186
24	228	226	9
26	217	235	171

H,6,2

0	786	751	198
1	655	648	182
2	819	815	26
3	538	521	25
4	829	787	339
5	303	320	17
6	995	1001	178
7	135	114	7
8	338	358	82
9	581	612	170
10	453	471	114
11	392	390	352
12	303	319	186
13	425	408	169
14	309	265	160
16	816	797	15
17	834	812	158
18	292	250	211
19	236	237	156
20	368	320	199
22	814	799	24
24	200	212	198
26	199	196	193

H,7,2

1	734	693	166
2	319	302	306
3	1064	1029	3
4	428	441	19
5	755	719	222
7	586	614	165
9	509	492	37
10	506	518	206
11	253	211	322
12	361	351	169
13	607	592	195
14	230	219	118
15	469	469	348
16	315	302	128
17	221	243	10
19	529	516	202
22	204	164	165
23	349	331	2
25	379	381	192

H,8,2

0	930	986	185
1	493	462	312
2	572	566	12
3	301	269	315
4	307	294	25
5	181	198	109
6	477	481	177
7	175	176	355
9	212	253	155
10	630	630	5
11	641	619	181
12	358	359	160
13	194	199	103
15	178	188	341
16	408	407	10
18	224	189	161
20	287	270	179
21	182	155	50
22	398	387	353

H,9,2

1	484	476	226
2	569	553	354
3	508	483	20
4	306	319	128
5	281	257	259
7	218	215	216
8	448	422	5
9	562	551	339

10	283	178	196
12	440	449	182
13	382	357	167
14	453	485	11
19	270	305	162
20	198	182	181
21	186	160	12

H,10,2

1	381	360	358
3	396	362	29
4	295	283	13
5	378	357	194
6	251	219	193
9	270	280	339
10	326	321	309
11	307	263	58
13	622	598	202
15	315	315	3
17	220	232	150

H,11,2

2	868	832	18
6	219	238	195
8	529	515	10
10	395	409	165
12	331	327	200
18	302	339	345

H,12,2

1	218	237	352
5	375	380	175
6	271	301	13
7	275	302	181
11	358	385	182
12	205	208	282

H,13,2

3	255	288	303
5	301	319	210
7	281	327	351
9	194	246	161

H,0,3

4	552	676	116
6	837	937	306
8	500	552	240
10	702	727	125
12	1199	1307	107
14	670	732	268
16	681	685	17
18	753	731	183
20	471	466	277
22	511	480	231
24	926	892	91
26	306	298	302
28	207	202	212

H,1,3

3	852	888	274
4	300	167	271
5	838	872	147
6	851	817	265
7	572	551	301
8	877	882	333
10	624	630	85
11	1301	1481	88
12	758	762	293
13	381	407	205
14	206	175	79
15	652	708	285
16	500	496	83
17	392	415	87
18	372	364	252
19	246	262	248
20	420	423	236
21	655	605	279
23	368	380	108
25	860	818	77
27	392	367	268
28	206	202	88
29	116	149	107

H,2,3

1	1700	1559	111
3	438	369	86

5	150	185	109
6	115	124	26
7	751	735	316
8	888	933	296
9	587	621	118
10	473	536	65
11	378	378	181
12	437	519	51
13	830	859	275
14	263	315	218
15	853	862	91
16	549	564	276
17	265	258	51
18	517	491	85
19	621	589	257
20	539	511	337
23	416	413	99
24	426	392	102
25	510	467	262
29	289	300	96

H,3,3

0	1611	1581	289
1	521	455	312
2	225	122	235
3	1259	1148	299
4	1129	1194	98
5	1176	1142	75
6	1262	1271	277
7	640	629	219
8	347	379	21
9	563	559	288
10	978	962	124
11	167	155	19
12	709	731	299
13	491	516	77
14	239	261	146
15	251	292	241
16	769	767	77
18	279	284	299
20	328	328	280
22	869	882	68
25	286	288	137
26	405	382	281
28	296	298	99

H,4,3

1	598	592	256
2	382	398	169
3	1148	1148	78
4	522	457	319
5	535	506	272
7	1802	1822	271
8	510	525	59
9	761	820	108
10	198	191	203
11	203	158	20
12	276	271	122
13	868	825	108
14	275	118	86
15	828	888	187
16	273	292	241
17	612	612	68
18	246	266	285
19	828	778	255
20	218	85	81
21	267	289	54
25	222	208	281

H,5,3

0	582	537	234
1	512	476	128
2	723	696	88
3	330	292	87
4	812	781	77
5	1639	1559	257
6	1028	1008	267
7	711	641	95
8	499	506	301
9	833	817	61
10	908	913	98
11	273	301	208
12	852	866	279
13	268	313	175
15	263	229	99
16	696	671	91
17	661	685	257
20	300	295	270
21	291	264	124

Table 2.7 continued

H,5,3

23	255	234	301

H,6,3

1	169	163	313
2	908	876	75
3	852	800	95
4	916	871	287
5	369	373	267
6	548	557	233
7	379	369	299
8	1075	1049	88
10	147	145	288
11	224	242	82
12	587	607	265
13	359	358	269
14	607	591	88
15	512	502	102
18	505	840	288
17	295	234	296
20	385	295	119
24	201	169	313
25	287	278	266
26	177	192	101

H,7,3

0	278	233	83
1	917	909	80
2	316	293	113
3	366	363	6
4	263	266	286
5	790	768	263
6	268	302	311
7	890	837	136
8	262	221	251
9	568	600	59
11	767	787	267
12	285	290	285
13	810	824	81
14	333	350	71
15	850	838	105
17	363	342	263
21	316	286	95
23	256	230	311
25	131	129	212

H,8,3

1	875	835	88
2	633	605	94
3	824	850	218
4	710	690	103
5	268	262	102
7	234	230	149
8	360	339	114
9	361	335	289
10	189	200	276
11	245	219	234
12	413	373	274
13	521	522	108
14	626	612	81
16	308	310	236
18	292	257	285
20	299	279	105
23	132	155	283

H,9,3

0	875	898	70
1	313	287	124
2	282	274	239
3	215	199	186
4	211	206	289
5	329	290	298
6	212	210	66
7	823	798	102
10	488	462	280
11	873	862	268
12	309	305	93
13	261	248	86
14	263	246	89
17	316	324	266
21	271	246	92
22	269	303	259

H,10,3

1	326	317	95
3	167	179	252
7	288	246	110
9	530	506	287
10	273	277	251
13	815	828	99
15	250	239	273
18	186	178	256
19	385	383	65
20	218	227	86

H,11,3

0	272	232	89
3	256	235	109
8	329	338	289
6	848	850	82
8	314	302	243
10	298	276	101
12	305	301	108
14	151	194	87
16	349	386	263

H,12,3

1	246	211	96
3	213	207	245
7	170	196	102
8	225	244	250
9	360	381	257
10	199	211	88
13	269	304	91
16	119	174	242

H,13,3

0	383	386	79
1	188	175	291
4	179	200	258
5	275	292	97
7	221	248	260

H,0,4

4	1013	871	142
6	328	260	45
8	533	476	245
10	1599	1708	176
12	1615	1773	355
14	212	256	70
16	779	827	177
18	320	331	27
20	316	324	311
22	699	701	190
26	512	550	1
28	272	308	170

H,1,4

2	883	738	195
3	1197	1099	202
4	991	925	348
5	872	838	69
6	627	598	163
7	273	305	298
8	828	850	218
9	610	673	194
10	290	297	18
12	253	283	351
13	1124	1191	0
14	698	728	193
15	510	560	169
16	389	369	8
17	382	325	225
18	259	216	24
19	657	639	13
20	422	392	218
21	285	292	216
22	255	246	174
23	686	601	178
24	468	417	2
25	537	440	19
26	303	273	172

H,2,4

0	1903	1689	88
1	1081	977	153
3	568	522	261
5	766	694	6
6	677	666	13
7	484	417	179
9	359	339	197
10	619	601	169
11	861	901	15
12	508	536	7
13	645	694	207
14	816	881	20
15	328	351	161
16	404	428	179
17	959	980	1
18	831	358	11
21	469	456	175
22	529	871	194
23	381	359	339
26	223	210	0
27	409	389	187

H,3,4

1	787	748	50
2	855	835	162
3	675	684	189
4	1402	1317	350
5	748	693	217
6	369	360	19
8	1005	1001	188
9	322	368	166
10	286	330	32
11	270	270	211
12	277	268	24
13	281	269	7
14	511	519	185
15	818	809	2
16	296	296	128
17	215	216	119
18	888	856	358
20	632	566	161
24	313	290	355
26	269	247	169
28	159	186	198

H,4,4

1	963	926	170
2	599	581	41
3	662	585	152
4	296	285	291
5	2002	1902	2
6	895	850	213
7	525	513	163
9	792	755	206
10	263	251	283
11	577	559	26
12	230	227	161
13	220	192	248
14	305	259	32
15	660	658	166
16	269	268	6
17	569	560	358
20	236	186	252
21	539	531	159
23	266	237	335
27	313	309	186

H,5,4

1	850	819	257
2	1175	1078	173
3	769	711	15
4	1169	1122	355
5	348	301	327
6	746	743	86
7	825	807	163
8	837	805	200
9	582	570	319
10	411	394	291
11	197	190	125
12	370	359	330
14	374	385	201
15	268	280	330
18	675	651	355
19	463	398	183
26	228	218	191

H,6,4

0	1067	958	201
1	588	530	170
2	807	822	52
3	378	333	3
4	808	771	358
5	532	509	20
6	1040	1018	173
7	188	193	193
8	172	194	182
9	537	531	187
10	546	551	359
11	362	336	342
12	509	545	135
13	851	861	176
14	290	303	221
15	246	218	149
16	808	806	356
17	881	865	0
18	270	229	150
20	191	212	218
26	120	176	147

H,7,4

1	888	879	182
3	905	838	8
4	343	302	15
5	303	292	219
6	331	332	235
7	722	699	171
8	162	185	170
9	562	610	5
10	258	240	121
11	329	331	28
12	238	208	178
13	660	668	186
14	281	307	169
15	551	551	338
16	381	387	335
17	236	199	88
18	251	218	38
19	239	207	208
23	297	268	350

H,8,4

0	841	807	180
1	736	677	349
2	817	379	28
3	314	303	38
4	178	136	337
6	833	831	186
8	214	200	98
10	859	868	381
11	201	192	168
12	612	602	172
15	205	195	3
16	833	889	10
18	209	228	168
20	185	185	197
22	349	333	7
23	140	149	151

H,9,4

2	560	536	356
3	836	825	387
7	271	288	154
8	358	325	37
9	831	800	338
10	281	296	252
12	826	393	193
13	340	325	178
14	817	819	11
15	263	242	18
19	388	396	189
20	178	198	388
21	183	180	5

H,10,4

1	835	817	338
4	286	288	3
5	359	323	183
7	367	340	26
8	238	218	338
11	522	535	199
12	217	217	198
15	327	330	352
17	350	342	183
18	138	150	210

H,11,4

2	392	816	367
8	296	267	2
10	377	396	186
18	279	269	12

H,12,4

1	249	210	350
3	216	283	17
5	291	283	172
6	201	227	388
7	230	211	350
11	258	250	177
12	168	201	351

H,13,4

2	292	252	7
3	210	222	208
7	239	281	186
8	120	188	6

H,0,5

2	1105	1025	282
4	1136	1053	115
6	659	631	8
8	1212	1188	295
10	1053	1065	107
12	1212	1261	75
14	881	940	267
16	237	307	55
18	288	279	128
20	420	389	281
22	273	229	268
24	575	587	93
26	224	196	262
28	190	214	282

H,1,5

0	1008	856	282
1	856	805	271
2	1136	983	56
3	960	765	269
4	350	342	95
5	562	613	76
6	403	369	246
7	428	408	297
8	295	300	200
9	828	821	238
10	356	391	61
11	1636	1640	83
12	883	867	285
13	360	328	260
14	182	183	180
15	416	401	272
16	252	220	80
17	803	809	107
18	371	352	116
19	250	283	273
20	272	230	255
21	550	520	278
22	279	261	128
23	355	313	117
25	363	336	90
26	181	199	287
27	326	295	260
28	179	200	91

H,2,5

1	579	552	251
4	828	781	272
5	960	824	271
6	712	686	55
7	510	585	250
8	903	852	257
9	305	328	149
10	508	462	82
11	308	315	18
12	383	331	111
13	617	658	260
14	417	464	270
15	575	546	108
17	331	312	75
18	458	448	17
19	653	587	279
20	500	430	271
23	398	386	95
24	322	278	96
25	483	416	260
27	191	180	50
28	178	197	231

H,3,5

0	1253	1171	289
1	585	606	325
2	872	881	99
3	1180	1081	271
4	915	919	86
5	506	482	120
6	522	558	21
8	581	606	269
10	1681	1753	169
12	727	803	186
18	309	239	82
22	395	366	203
26	385	388	3

H,4,5

0	1816	1295	58
1	1106	1047	178
2	213	218	198
3	198	284	296
4	635	574	183
5	666	637	0
6	827	788	345
7	215	267	168
8	504	477	188
9	510	509	110
10	806	808	198
11	277	294	350
12	482	512	11
13	259	270	279
14	226	228	88
15	811	832	203
16	320	306	186
17	369	365	21
18	362	318	315
21	308	325	199
22	870	848	184
26	269	288	389
27	271	258	190

H,5,5

0	871	847	81
1	287	276	73
2	343	312	288
4	206	213	359
5	490	460	245
6	207	201	121
7	300	288	71
9	261	269	65
10	398	397	277
11	378	376	265
12	322	336	98
14	295	288	80
17	337	325	299
20	130	169	83
21	273	326	107

H,6,5

1	597	582	57
2	641	606	178
3	422	381	290
4	1192	1129	319
5	260	310	180
7	329	318	87
8	900	937	178
9	576	568	192
10	315	308	329
11	316	321	327
12	468	506	2
14	488	488	205
17	231	250	17
18	710	758	159
19	348	329	330
20	552	538	152
21	386	382	171
24	320	316	4
26	258	275	191
27	166	173	382

H,7,5

0	868	892	158
1	719	665	107
2	177	145	66
4	659	648	128
8	250	288	351
5	685	636	270
6	218	216	227
7	259	230	69
8	267	256	218
9	360	388	78
11	768	780	259
12	215	211	233
13	413	431	53
15	453	438	108
16	277	261	117
17	375	360	264
21	200	187	98
23	160	165	292

H,8,5

1	629	607	119
2	577	531	65
3	395	350	293
4	385	398	258
5	259	233	314
6	231	230	226
7	318	338	202
8	569	588	95
9	165	172	290
10	300	112	272
12	838	889	259
13	321	319	99
14	638	603	87
16	214	187	281
18	238	246	298
20	196	199	110
22	183	125	96

H,9,5

0	871	847	81
1	287	276	73
2	343	312	288
4	206	213	359
5	490	460	245
6	207	201	121
7	300	288	71
9	261	269	65
10	398	397	277
11	378	376	265
12	322	336	98
14	295	288	80
17	337	325	299
20	130	169	83
21	273	326	107

H,10,5

1	248	237	72
2	369	387	87
3	505	526	249
9	872	867	286
11	182	212	206
13	822	805	106
17	127	183	238
18	151	179	258

H,11,5

0	553	536	91
4	388	382	263
6	371	389	74
9	209	208	308
10	215	209	270
12	209	311	116
14	206	224	68
16	267	305	271

H,12,5

1	283	314	102
3	295	308	290
6	210	221	52
8	237	284	288
9	280	286	266

H,1,6

1	1051	915	356
2	803	767	186
3	672	584	162
4	667	628	15
6	240	153	220
7	943	872	341
8	429	392	201
9	1160	1167	189
10	427	447	147
11	387	374	98
12	419	488	334
13	990	1073	358
14	343	357	170
15	281	250	159
21	283	273	295
23	342	303	193
24	257	245	156
25	297	255	353
26	291	259	162

H,2,6

0	1816	1295	58
1	1106	1047	178
2	213	218	198
3	198	284	296
4	635	574	183
5	666	637	0
6	827	788	345
7	215	267	168
8	504	477	188
9	510	509	110
10	806	808	198
11	277	294	350
12	482	512	11
13	259	270	279
14	226	228	88
15	811	832	203
16	320	306	186
17	369	365	21
18	362	318	315
21	308	325	199
22	870	848	184
26	269	288	389
27	271	258	190

H,3,6

1	597	582	57
2	641	606	178
3	422	381	290
4	1192	1129	319
5	260	310	180
7	329	318	87
8	900	937	178
9	576	568	192
10	315	308	329
11	316	321	327
12	468	506	2
14	488	488	205
17	231	250	17
18	710	758	159
19	348	329	330
20	552	538	152
21	386	382	171
24	320	316	4
26	258	275	191
27	166	173	382

H,4,6

0	870	807	23
1	885	770	193
2	359	319	231
3	500	499	83
4	836	840	326
5	1283	1248	8
6	517	481	182
7	915	906	159
8	887	887	149
9	385	358	263
10	298	252	21
11	368	369	388
15	678	676	165
16	313	294	36
17	719	729	5
21	658	609	171
23	398	396	346

H,5,6

2	548	481	177
3	491	465	21
4	743	692	12
5	330	337	339
6	520	514	25
7	787	727	202
8	518	486	198
9	319	323	312
10	229	213	293
11	336	331	110
13	238	236	218
14	636	657	173
15	364	387	3
18	616	600	349
19	501	457	180
20	388	350	157
24	350	326	337

H,6,6

0	334	330	221
1	480	436	171
2	247	249	134
3	331	292	339
4	681	668	28
5	228	198	11
6	625	599	185
7	208	229	231
9	388	390	179
10	535	558	19
11	215	211	238
12	567	611	170
13	246	179	168
14	193	188	243
16	538	497	356
17	309	265	5
18	387	360	162
22	262	255	350

H,7,6

1	198	166	202
2	409	388	55
3	515	514	359
5	255	232	116
7	716	691	181
9	753	747	358
10	248	241	166
11	259	263	358
13	712	698	173
15	653	670	351
19	289	269	175
20	270	252	383
21	309	308	388

H,8,6

0	739	691	159
1	535	506	22
2	309	291	315
3	261	273	116
4	286	270	349
5	219	207	109
6	508	498	182
8	176	200	180
10	688	626	340
11	223	212	208
12	487	488	178
14	335	339	10
20	183	191	187
21	248	250	388
22	218	213	17

H,9,6

2	495	517	5
3	812	795	111
4	348	338	170
7	812	799	163
8	295	263	16
10	265	277	212
12	392	401	165
13	293	264	180
16	301	307	149
17	221	162	388
19	191	203	199
20	179	198	18

H,10,6

1	657	618	358
4	391	379	385
5	358	362	168
7	308	309	7
11	868	842	181
15	308	299	353

H,11,6

2	598	589	356
4	280	318	181
8	340	388	389
10	232	215	282
12	252	288	177

H,12,6

1	321	329	16
4	315	320	159
5	298	295	165
6	288	278	1
11	256	272	188

H,0,7

4	1035	1007	71
6	989	998	131
8	1220	1234	295
10	561	608	122
12	1069	1167	88
14	881	946	278
20	281	286	312
24	299	327	89
26	223	228	231

H,1,7

0	837	758	230
1	1179	1077	287
2	869	817	159
3	513	497	300
4	828	803	87
5	688	686	86
6	386	401	352
7	866	896	241
8	840	807	219
9	517	509	255
10	331	334	92
11	1077	1124	98
14	298	315	297
15	303	294	277
21	324	276	278
25	268	280	102

H,2,7

1	758	715	297
2	902	852	248
3	1008	962	76
4	283	275	388
5	558	512	281
6	286	210	113
7	690	678	279
8	571	553	293
9	303	335	106
10	621	680	91
11	345	401	78
12	221	248	188
13	520	545	269
14	815	868	239
17	288	294	89
19	381	369	289
20	835	797	261
24	355	382	108
25	352	387	278

H,3,7

0	781	765	282
1	319	271	116
2	825	808	112
3	829	829	264
4	718	681	78
5	815	788	2
6	1108	1087	273
7	589	609	259
8	336	318	95

Table 2.7 continued.

H,3,7

9	471	505	80
10	356	352	89
12	317	319	217
14	247	316	270
15	278	276	249
16	757	761	86
17	250	245	17
20	413	415	264
21	332	156	278
22	471	440	93
26	225	218	275

H,4,7

1	299	294	211
2	219	225	67
3	918	920	110
4	240	259	117
5	828	803	285
6	318	293	257
7	641	712	279
8	294	286	120
9	687	743	76
11	291	315	216
15	531	545	106
17	832	873	87
19	930	816	269
21	319	328	68
25	394	368	283

H,5,7

0	510	493	267
2	878	865	117
3	391	372	59
5	551	558	260
6	732	709	292
7	370	348	70
9	377	360	101
16	672	648	97
17	520	488	268
20	881	897	281
22	885	838	77

H,6,7

2	269	218	68
3	321	308	73
4	241	215	258
6	803	798	249
7	873	860	285
8	771	741	86
10	888	853	293
12	327	363	108
13	383	391	253
14	567	621	86
15	292	323	96
16	298	310	278
18	376	353	255
20	357	387	80
23	179	158	56
24	395	370	270

H,7,7

1	809	869	68
2	288	286	76
3	253	241	210
4	249	213	138
5	467	453	288
7	227	256	132
8	298	307	238
9	803	862	92
11	756	769	269
12	198	228	129
13	295	281	85
15	309	317	86
17	835	820	270
21	275	262	85
22	190	179	268

H,8,7

1	195	201	97
2	861	881	86
3	275	261	265
4	369	347	265
5	203	197	103
6	283	286	249
7	220	215	231
8	648	681	105
9	208	206	282
10	171	176	265
12	815	832	262
13	250	256	77
14	898	880	83
19	203	220	88
21	125	161	300

H,0,8

2	299	283	168
4	883	863	215
6	681	640	359
10	1212	1105	193
12	818	861	2
16	529	593	175
22	298	260	189
26	257	293	355

H,1,8

1	817	816	20
2	828	752	190
3	937	899	167
4	280	216	3
5	270	240	212
6	290	300	99
7	776	788	18
8	349	329	199
9	919	981	189
12	328	337	7
13	838	868	11
14	371	423	157
15	393	387	175
16	311	278	260
19	299	258	180
23	362	326	194
24	265	250	321
25	260	225	389

H,2,8

0	595	589	351
1	986	920	187
4	913	886	159
5	867	815	29
6	560	513	322
7	391	350	216
8	298	305	181
9	812	822	179
10	345	346	220
11	885	881	326
12	376	398	21
13	298	331	100
15	881	919	196
16	338	338	152
17	266	296	5
18	819	836	342
21	349	335	185
22	818	890	196
23	221	207	10
26	238	244	27

H,3,8

1	841	823	355
2	839	777	199
3	286	218	88
4	1079	1011	23
5	187	209	152
6	820	800	342
7	856	855	268
8	689	679	177
9	295	302	185
10	225	269	347
11	326	353	356
12	269	263	328
13	839	851	60
14	309	331	198
18	687	671	7
20	829	820	176
24	312	278	9

H,4,8

1	710	689	188
3	320	307	69
5	925	911	382
6	193	358	175
7	545	600	170
8	314	336	172
11	853	858	330
15	818	895	167
17	657	692	8
21	528	503	198
23	368	376	7

H,5,8

2	632	580	335
4	618	521	29
6	335	326	292
7	888	831	189
8	583	534	183
14	540	591	170
18	572	525	19
24	225	226	358

H,6,8

0	858	851	112
1	802	805	156
3	358	316	349
4	877	816	332
5	338	306	53
6	435	399	177
7	278	281	236
8	165	215	318
9	883	861	178
10	824	821	19
12	859	870	203
16	512	508	359
17	252	256	15
18	253	254	218
21	234	219	182
22	270	277	358

H,7,8

2	217	196	268
3	501	892	358
4	275	264	13
5	280	289	137
6	368	372	50
7	878	883	178
8	178	197	228
9	567	570	5
11	283	278	301
13	522	527	171
15	888	887	13
19	292	279	184
20	196	161	19

H,8,8

0	759	703	186
1	183	208	139
2	308	329	327
4	331	287	26
5	203	215	70
6	831	875	187
10	863	873	5
12	806	801	190
16	301	308	349
20	157	189	158

H,0,9

2	1137	1085	290
4	728	657	32
6	708	659	155
8	587	559	283
10	558	549	82
12	508	526	88
14	651	696	249
18	290	321	69
20	312	318	262
22	218	198	229
24	938	889	80

H,1,9

0	773	676	273
1	813	712	263
2	386	333	68
3	871	805	336
5	726	707	93
6	383	350	300
7	572	516	250
10	722	319	79
11	807	829	98
12	847	520	229
15	901	859	278
16	271	269	94
17	365	421	69
21	392	362	259
23	275	238	72

H,2,9

1	330	307	286
2	742	681	234
3	722	688	106
5	315	281	267
6	370	404	38
7	808	797	241
8	575	519	268
9	842	826	56
10	341	313	111
12	352	358	126
13	513	545	245
15	371	414	50
18	260	279	66
19	378	373	272
20	395	401	259
23	314	279	62
24	286	274	118
25	298	275	253

H,3,9

0	903	853	282
1	326	312	203
2	553	541	132
3	607	629	251
4	749	681	73
5	625	599	7
6	695	668	273
7	772	786	280
10	870	897	83
12	817	803	241
16	513	535	89
18	293	311	270
20	333	326	289
22	397	358	97

H,4,9

1	332	276	272
3	752	735	105
5	477	503	342
6	317	326	293
7	693	681	246
9	892	900	69
13	356	360	288
15	367	404	115
17	885	860	95
19	897	885	289

H,5,9

0	698	602	252
2	586	567	104
3	842	797	62
4	333	257	65
5	524	472	253
6	727	689	264
7	376	367	58
10	379	362	72
12	326	374	294
16	882	898	108
20	316	282	290

H,6,9

2	870	842	72
3	368	387	82
4	372	340	233
5	229	239	292
6	231	203	242
7	383	332	271
8	511	502	88
10	241	268	106
12	277	266	250
13	379	419	222
14	424	429	130
15	259	276	82
16	252	268	381
18	344	327	258
19	216	201	301
20	189	163	98

H,7,9

1	588	588	68
3	288	264	178
5	591	597	286
7	279	278	101
9	246	242	110
11	576	600	276
13	265	277	150
15	275	258	62
17	369	370	298

H,8,9

2	890	855	187
4	303	335	260
6	282	303	300
7	250	226	155
8	316	380	100
12	241	237	260
13	220	235	79
14	371	438	81
18	181	212	263

H,0,10

0	956	893	155
2	585	509	115
4	762	787	262
6	307	272	351
8	261	201	187
10	526	533	174
12	507	577	358
16	360	401	168
20	326	339	323
22	881	539	179

H,1,10

1	353	336	10
2	321	300	193
3	663	612	187
5	836	814	313
9	520	528	185
13	922	865	5
14	927	886	151
19	373	396	388
23	378	381	180

H,2,10

0	595	518	310
1	399	358	215
4	881	862	166
5	378	411	31
6	885	831	339
7	801	829	186
9	267	259	166
10	393	466	208
11	516	518	333
12	289	336	53
13	306	350	140
14	373	415	3
15	276	278	180
17	173	208	8
21	291	291	185
22	338	330	160
23	193	177	16

H,3,10

1	319	320	0
2	881	880	192
3	300	305	171
4	687	627	17
6	501	506	317
7	337	331	208
8	633	635	154
10	295	318	329
13	333	367	11
14	417	448	194
15	279	280	300
18	855	868	18
20	292	307	185

H,4,10

1	861	876	212
3	868	863	120
5	877	895	300
9	390	404	187
11	396	431	358
17	357	361	8

H,5,10

2	529	504	158
3	865	820	351
4	620	548	26

H,8,10

7	874	850	186
8	628	641	163
9	889	864	14
18	307	307	31

H,6,10

0	597	615	183
1	253	268	148
2	321	315	336
4	556	562	355
5	328	368	32
6	573	596	189
9	278	289	183
10	373	363	14
11	276	274	301
12	318	305	236
14	241	200	121
16	338	332	356
17	212	203	7

H,7,10

1	315	331	175
3	611	608	355
5	232	226	121
7	366	364	192
9	271	265	1
11	197	179	298
13	359	350	161
15	246	223	10
16	186	158	383
19	223	251	196

H,8,10

0	813	849	162
1	288	296	8
2	266	289	321
4	262	269	56
6	275	278	187
9	266	295	311
10	312	333	0
11	282	255	182
12	264	302	101
15	126	139	33
16	292	322	355

H,0,11

2	507	557	297
4	820	818	51
8	288	244	299
10	323	339	146
12	311	383	61
14	335	352	272
18	315	339	83
20	420	429	282
22	189	162	282

H,1,11

1	588	535	259
3	365	380	2
6	276	325	298
8	220	175	178
10	310	332	88
11	570	569	111
12	262	300	281
15	317	353	269
18	260	259	277
21	436	417	269
22	216	221	109

H,2,11

2	599	603	271
3	357	363	99
7	226	219	258
8	832	851	256
9	881	873	93
10	245	298	103
12	370	458	125
13	303	441	251
14	251	257	286
15	383	392	85
16	257	292	248
18	284	288	88
19	235	261	298
20	249	260	255

H,3,11

0	278	233	250
2	275	274	176
4	483	471	65
6	606	605	275
10	425	433	90
11	305	323	126
12	309	305	257
16	393	406	97

H,4,11

3	668	677	102
5	317	316	321
7	755	802	268
9	523	511	68
19	328	305	268

H,5,11

0	369	318	291
4	551	539	98
5	559	555	253
6	641	526	268
7	499	433	75
10	491	428	97
16	408	317	96

H,6,11

2	588	606	91
3	283	288	99
4	527	517	265
8	406	406	97
12	263	288	258
13	259	237	210
14	218	223	110
15	213	188	76
18	283	277	247
19	138	169	319

H,7,11

0	306	350	153
1	535	555	73
5	463	501	209
9	255	288	111
11	337	350	264
15	202	197	78
17	203	248	269

H,8,11

2	292	308	80
4	383	422	259
7	183	206	78
8	209	220	113
10	133	169	315
12	196	158	273
13	208	219	79
19	243	282	76

H,0,12

0	1132	1090	359
2	440	432	185
4	356	382	158
6	297	261	353
8	291	267	260
10	338	340	157
12	330	348	28
16	344	368	172
18	253	280	22
20	286	291	381

H,1,12

1	381	368	159
3	506	518	179
9	437	457	213
13	350	385	11
19	395	376	359

H,2,12

0	623	615	38
1	384	400	146
5	805	812	16
6	346	340	335
7	249	241	213
9	309	292	144
10	299	312	228
11	387	411	385
12	262	290	17
14	250	248	5
16	237	202	186
17	356	368	26
21	193	203	208

H,3,12

1	328	286	62
2	399	436	183
3	318	313	212
4	303	287	17
6	317	335	368
8	540	525	176
10	275	305	338
14	423	462	180
18	280	271	0
20	191	173	176

H,4,12

5	617	624	358
11	369	402	351
17	279	297	348

H,5,12

3	458	390	8
4	811	317	20
6	381	297	30
8	497	423	190
18	378	291	167
17	293	191	319
18	251	214	8

H,6,12

0	427	417	180
1	272	282	138
4	282	312	3
5	302	375	39
6	382	410	187
10	231	263	26
11	258	242	329
16	239	263	353
17	192	217	33

H,7,12

1	291	383	183
3	419	456	355
7	219	219	216
13	231	227	180
15	170	181	333

H,8,12

0	336	378	158
2	235	268	341
6	260	305	171
10	212	244	342
11	168	239	196
12	118	152	186
13	115	162	299

H,0,13

2	726	698	268
4	568	570	55
8	389	381	277
10	312	371	153
12	331	381	85
14	251	268	278
18	257	283	98

H,1,13

0	490	456	210
1	650	669	270
5	884	886	71
7	325	345	298
10	290	306	58
11	319	325	101
15	290	298	264
17	250	255	76

H,2,13

2	803	802	286
3	375	361	72
7	361	384	276
8	289	268	251
9	295	310	97
13	310	308	251
15	265	298	113
18	229	235	85
19	160	175	321

H,3,13

0	380	377	285
4	295	314	78
6	411	445	274
10	375	398	83
12	321	358	273
16	380	386	86

H,4,13

7	831	860	277
8	351	385	172
15	275	309	98

H,5,13

10	386	329	98
12	439	385	246
16	261	266	98

H,6,13

2	232	236	100
4	206	289	280
13	150	173	242

H,7,13

1	330	378	81
5	280	313	281
11	212	237	246

H,8,13

2	275	314	85
4	225	266	256
8	192	235	93
9	126	169	321

H,0,14

0	797	821	350
2	352	338	136
4	293	314	160
6	375	421	10
10	126	155	155
14	231	292	80
16	228	224	161

H,1,14

3	420	473	177
13	264	277	1

H,2,14

0	380	462	61
1	291	311	149
5	350	415	11
9	246	303	178
11	231	262	353

H,3,14

8	390	441	179
14	312	389	197

H,4,14

3	292	287	26
4	318	268	191
10	221	268	190

H,6,14

6	288	280	190

H,7,14

1	196	221	195
3	248	275	355

H,8,14

0	258	133	178
4	101	195	6

H,0,15

2	880	518	291
4	265	259	87
8	298	329	277
12	217	291	97
18	187	265	237

H,1,15

1	328	371	291
11	233	286	88

H,2,15

7	288	363	296

H,3,15

6	291	355	272
10	225	310	112

H,4,15

3	229	188	85
4	202	263	291

H,0,16

0	322	301	6
6	238	281	26
10	222	271	193

H,2,16

5	210	281	16

H,3,16

8	211	282	193

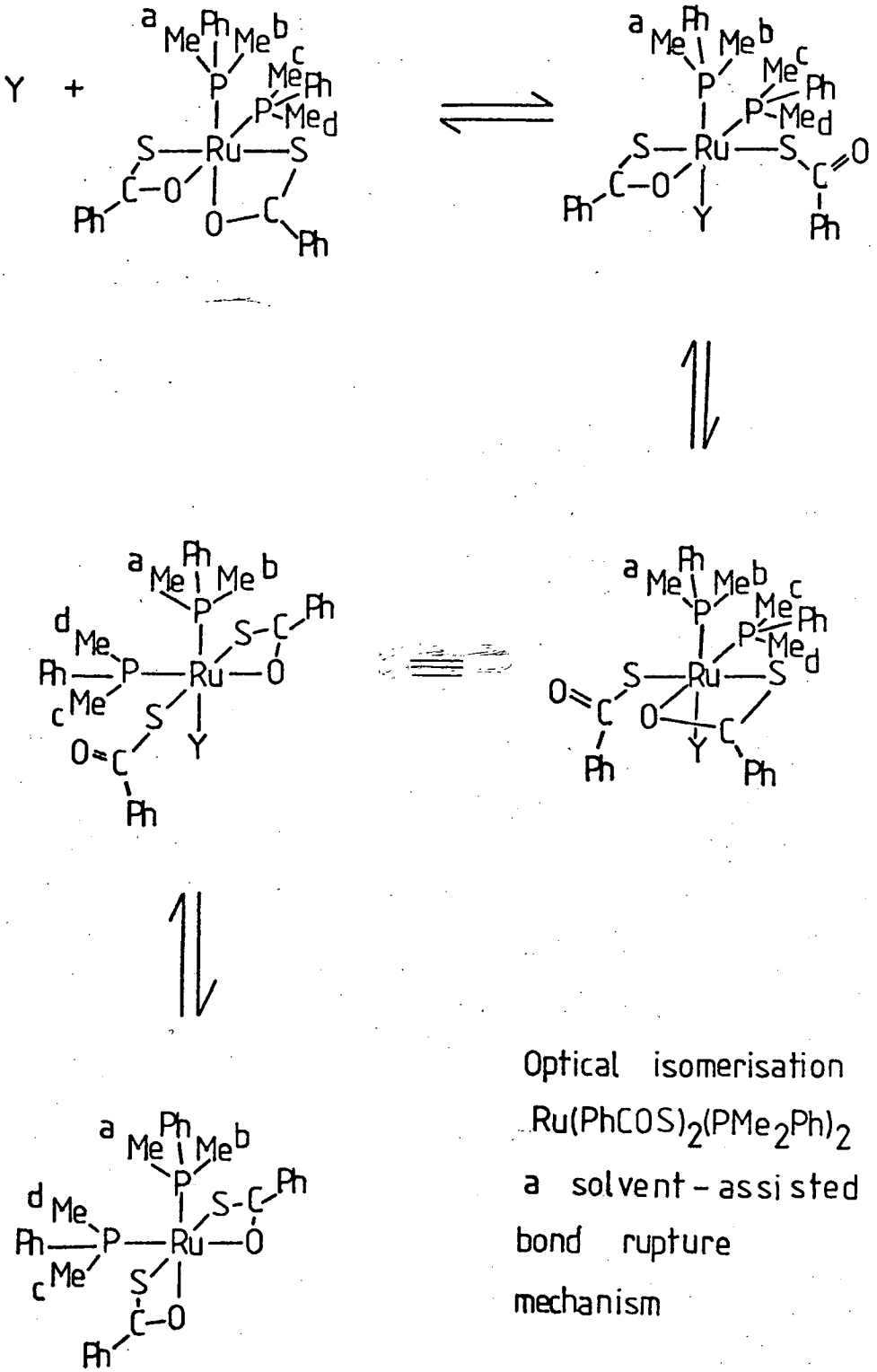
H,0,17

2	222	259	290

H,3,17

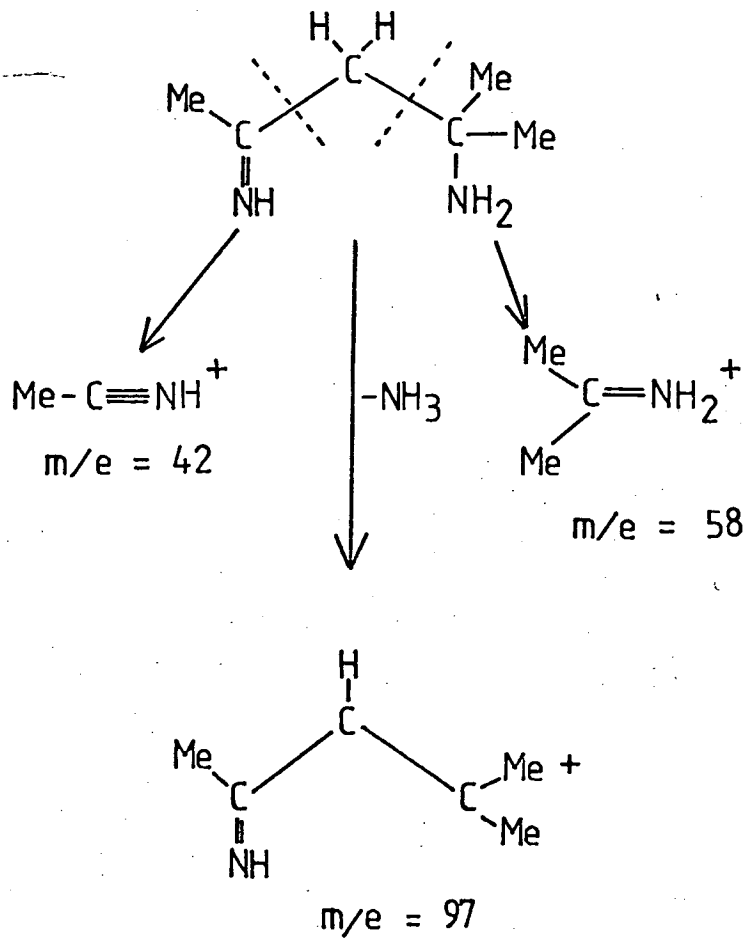
0	183	289	258

SCHEME 2.1



Optical isomerisation of $Ru(PhCOS)_2(PMe_2Ph)_2$ by a solvent-assisted bond rupture mechanism

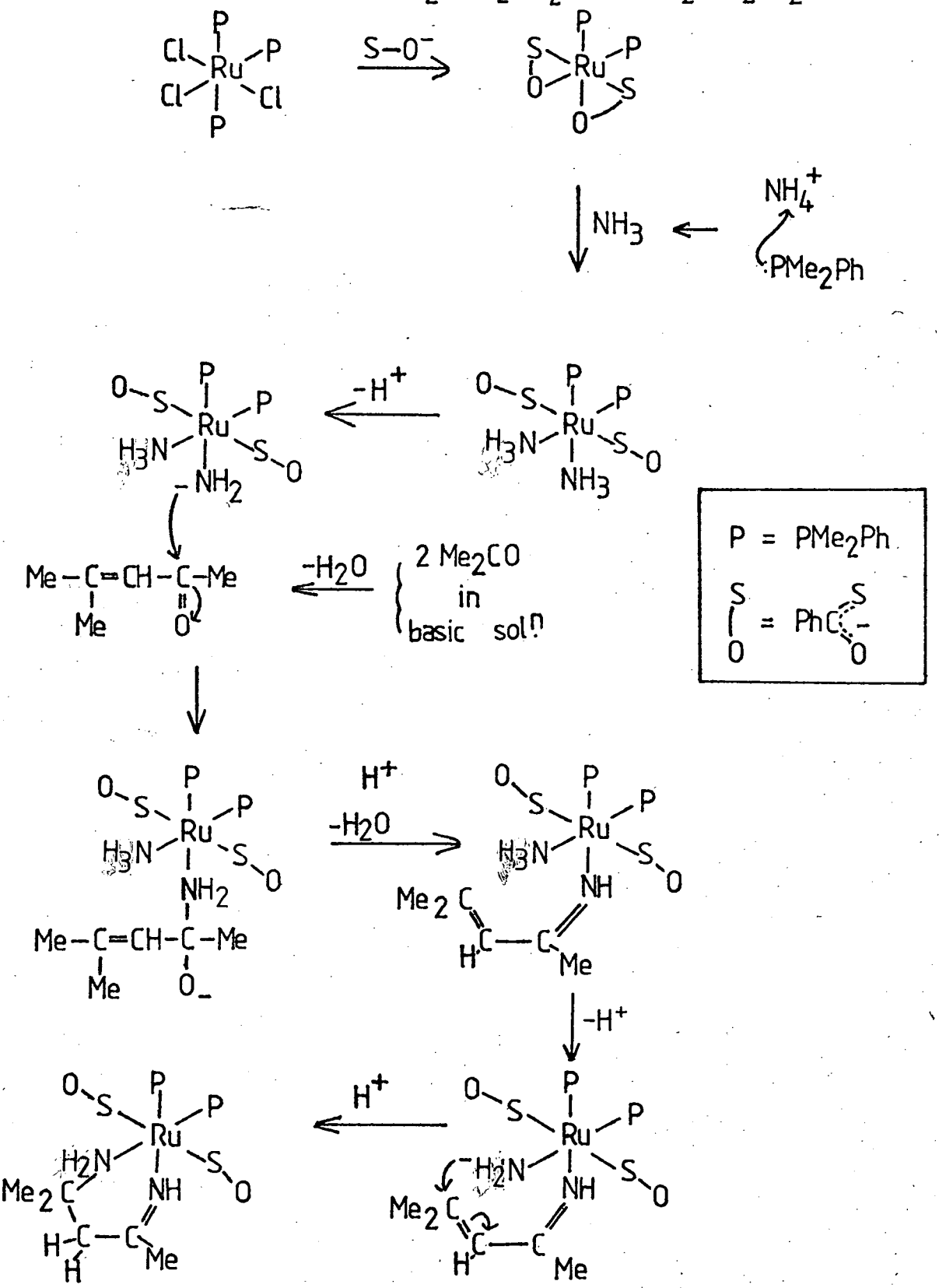
SCHEME 2.2



Proposed fragmentation pattern for 4-amino-2-imino-4-methylpentane

SCHEME 2.3

Proposed mechanism of formation of $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$



CHAPTER 3

REACTION OF $Ru(PhCOS)_2(PMe_2Ph)_2$ WITH VARIOUS BIDENTATE NITROGEN-DONOR LEWIS BASES, AND X-RAY ANALYSIS OF THE STRUCTURES OF SOME OF THE PRODUCTS

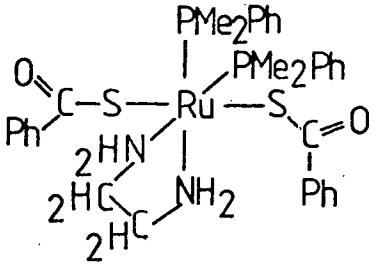
3(i) Introduction

The reaction of $Ru(PhCOS)_2(PMe_2Ph)_2$ with some monodentate nitrogen-donor bases such as NH_3 and NH_2Et gave products derived from the major isomer of the starting material (namely cis-$Ru(PhCOS)_2(PMe_2Ph)_2$) with the Lewis base cleaving the Ru-O bonds trans to the PMe_2Ph groups (see Chapter 2). In this Chapter, the results of extending these reactions to bidentate nitrogen donor bases such as ethylenediamine, 2,2'-bipyridyl and 1,10-phenanthroline are described.

3(ii) The Reaction of $Ru(PhCOS)_2(PMe_2Ph)_2$ with Ethylenediamine

When $Ru(PhCOS)_2(PMe_2Ph)_2$ was reacted with a 1:1 molar ratio of ethylenediamine in ethanol, a product was obtained which analysed for $Ru(PhCOS)_2(PMe_2Ph)_2(en)$ and, as expected, the i.r. spectrum indicates that the monothiobenzoate groups are bound through sulphur only. However, $\nu_{(CO)}$ at 1515 cm^{-1} is lower than might be expected, an observation which seems to be characteristic of monothiobenzoate complexes where there is scope for hydrogen-bonding of the uncoordinated acid oxygen to neighbouring ligands or co-crystallised solvent molecules; in this case the coordinated primary amine groups (cf. $(Ru(PhCOS)_2(PMe_2Ph)_2(NH_2Et)_2$, $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$ and references cited in Chapter 2).

In the ^{1}H-n.m.r. spectrum (see Table 3.1), a pseudotriplet pattern is observed at 1.69δ, and this pattern is preserved unchanged at low temperature, indicating as for the $Ru(PhCOS)_2(PMe_2Ph)_2L_2$ species discussed earlier, that the complex contains a plane of symmetry which makes the methyl groups on each phosphine magnetically equivalent at all temperatures. The pseudotriplet pattern decouples when irradiated at a frequency equivalent to a ^{31}P chemical shift of ca 26 p.p.m., in agreement with the ^{31}P-{^{1}H}-n.m.r. spectrum, which consists of a singlet at 21.72 p.p.m. Thus, the spectroscopic properties of $Ru(PhCOS)_2(PMe_2Ph)_2(en)$ are similar to those of the monodentate base adducts discussed in Chapter 2, and it can be assigned an analogous structure (28).



(28)

It is worth noting that the five-membered chelate ring trans to the phosphines in this case does not have the same effect of destroying the magnetic equivalence of the phosphine methyl groups as was observed at low temperature in the ^{1}H-n.m.r. spectrum of $Ru(PhCOS)_2(PMe_2Ph)_2$-$(HNCMeCH_2CMe_2NH_2)$ where a six-membered chelate ring is involved. This illustrates the greater stereochemical rigidity of the five-membered ring, and examination of a molecular model of the system confirms that the least strained configuration for the ring is planar, giving the required mirror symmetry to the whole molecule.

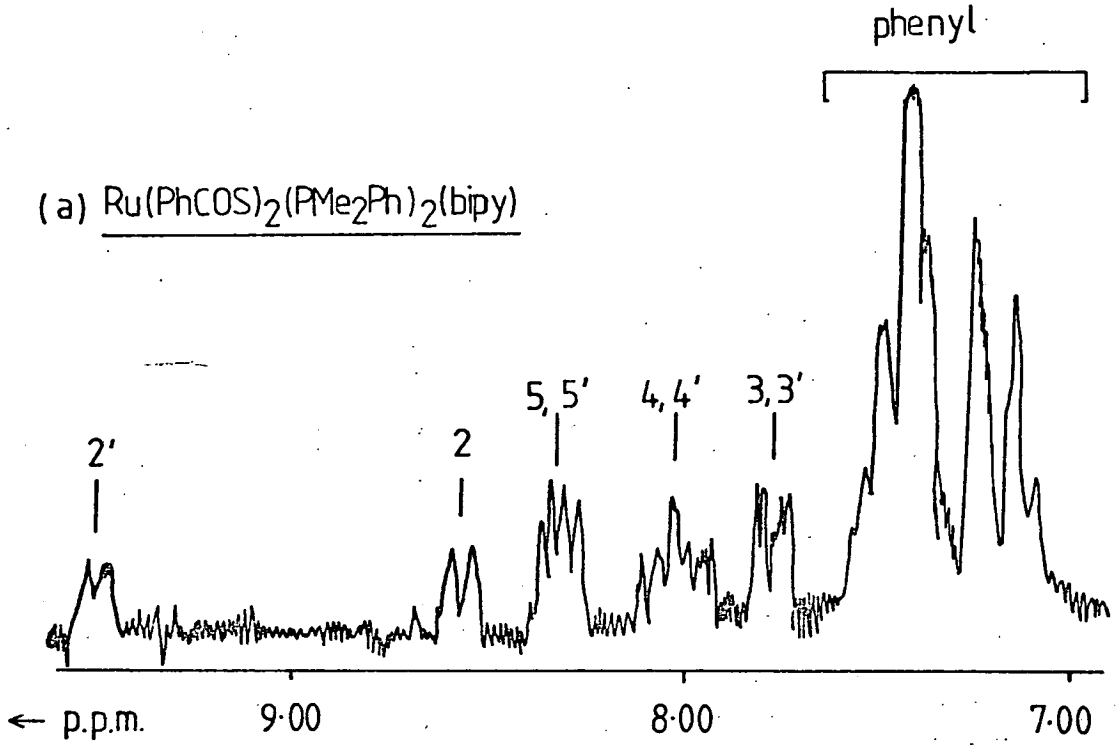
3(iii) The Reaction of $Ru(PhCOS)_2(PMe_2Ph)_2$ with 2,2'-bipyridyl and 1,10-phenanthroline

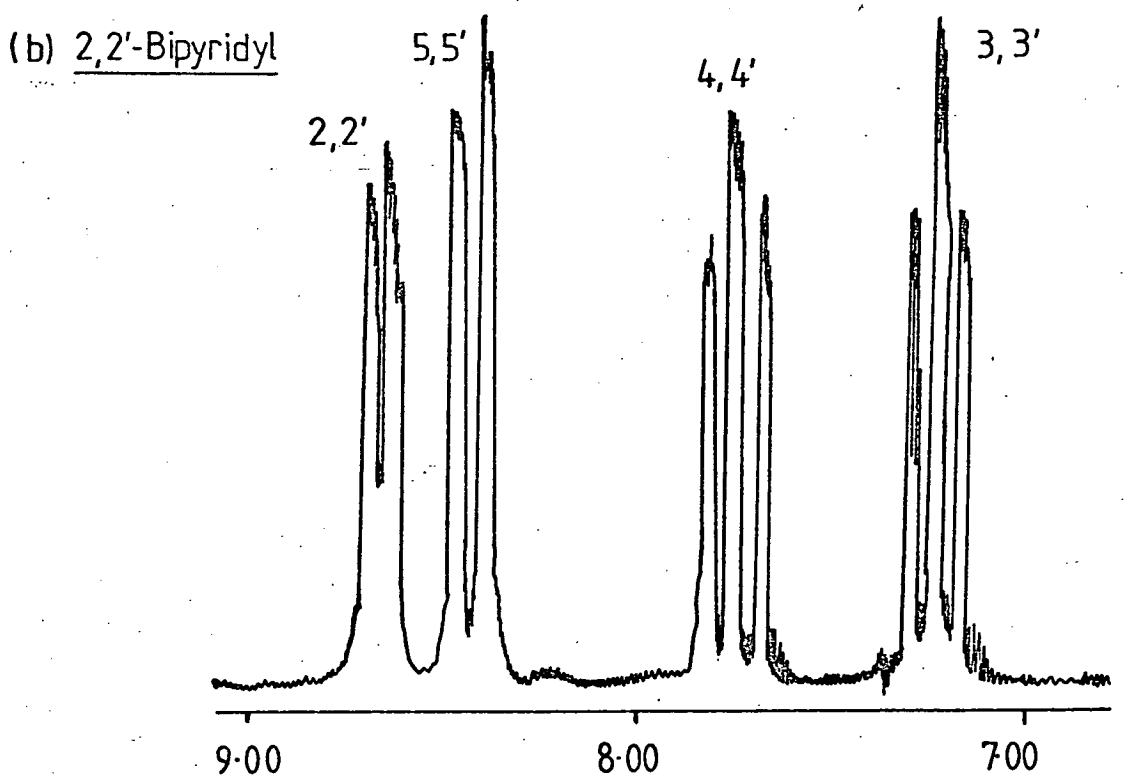
When $Ru(PhCOS)_2(PMe_2Ph)_2$ was reacted in 1:1 molar ratio with L_2 = 2,2'-bipyridyl or 1,10-phenanthroline, products analysing for $Ru(PhCOS)_2(PMe_2Ph)_2(L_2)$ were obtained as dark red crystals. Examination of the i.r. spectra indicates that in each case, as expected, the monothiobenzoate groups are coordinated in unidentate fashion through sulphur. Since these bidentate ligands both form five-membered rings on coordination, and the aromaticity of the 1,10-phenanthroline molecule will in any case constrain it to remain planar, the familiar temperature-independent pseudotriplet pattern was anticipated in the ^1H-n.m.r. spectra. However, the spectra obtained for both species (see Table 3.1) exhibit four doublets in the methyl region indicating inequivalent methyl groups on cis-phosphines. In the case of $Ru(PhCOS)_2(PMe_2Ph)_2(bipy)$, the four doublets at 1.37δ, 1.38δ, 1.98δ and 2.04δ all have $J_{(PH)}$, 8 Hz, and all decouple when irradiated at a frequency equivalent to a ^{31}P chemical shift of ca 12 p.p.m. In the $^{31}P-\{^1H\}$-n.m.r. spectrum, a singlet is observed at 14.05 p.p.m. (300K), which shifts to 15.28 p.p.m. at lower temperature (250K) with no sign of splitting into more than one resonance. In the ^1H-n.m.r. spectrum of $Ru(PhCOS)_2(PMe_2Ph)_2(phen)$, four doublets appear at 1.25δ and 1.34δ ($J_{(PH)}$, 9 Hz), at 2.06δ and 2.14δ ($J_{(PH)}$, 8Hz) and there is a small 1:2:1 triplet at 1.50δ. The doublets are attributed to the methyl groups on cis-phosphines, and all decouple at a ^{31}P chemical shift of ca 13 p.p.m. The 1:2:1 triplet is attributed to a species containing "virtually coupled" trans-phosphines, and decouples at a ^{31}P shift of ca 6 p.p.m. In the $^{31}P-\{^1H\}$-n.m.r. spectrum, an AB pattern is observed at 12.87 p.p.m. (δPP = 47.5 Hz, $J_{(PP)}$ = 30.8 Hz), clearly

arising from the complex containing inequivalent cis-phosphine groups which gives rise to the doublets in the ^{1}H-n.m.r., and a singlet appears at 5.73 p.p.m., arising from the trans-phosphine species associated with the triplet in the ^{1}H-n.m.r. spectrum.

In the aromatic region of the ^{1}H-n.m.r. spectra of the two complexes, resonances arising from the phenyl rings on the phosphines and the monothiobenzoate groups are superimposed between 7.00δ and 7.60δ. Resonances from the 2,2'-bipyridyl and the 1,10-phenanthroline ligands are also observed, and in each case the protons on the α-carbon atoms have become inequivalent (see Fig. 3.1). Uncoordinated, or symmetrically coordinated, 2, 2'-bipyridyl and 1,10-phenanthroline each shows four resonances arising from four pairs of symmetry-related protons (3.1b and 3.1d). However, when coordinated in an unsymmetrical environment, the symmetry is partially broken and the 2 and 2' protons in the bipyridyl, or the 2 and 9 protons in the phenanthroline, become inequivalent and give rise to separate resonances. This behaviour has been observed in tin[113] and ruthenium[114] complexes where the effect has been attributed to the influence of bulky neighbouring groups. In the present case, the inequivalence of the cis-phosphines in the principal isomer of $Ru(PhCOS)_2(PMe_2Ph)_2(phen)$ suggests that, in the phenanthroline adduct at least, the effect is due to the actual inequivalence of the coordinated nitrogens and taken together with the rest of the spectroscopic evidence, indicates that these bulkier bidentate ligands form adducts of an unexpected stereochemistry, containing inequivalent cis-phosphines (29) in the major species.

FIGURE 3.1 ^1H-n.m.r. spectra of $Ru(PhCOS)_2(PMe_2Ph)_2(L_2)$ 2,2-bipyridyl and 1,10-phenanthroline





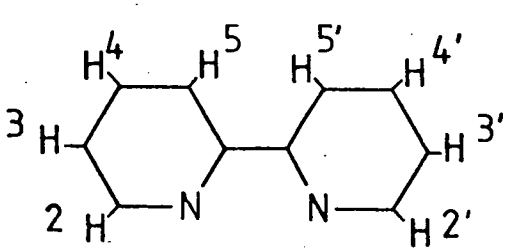
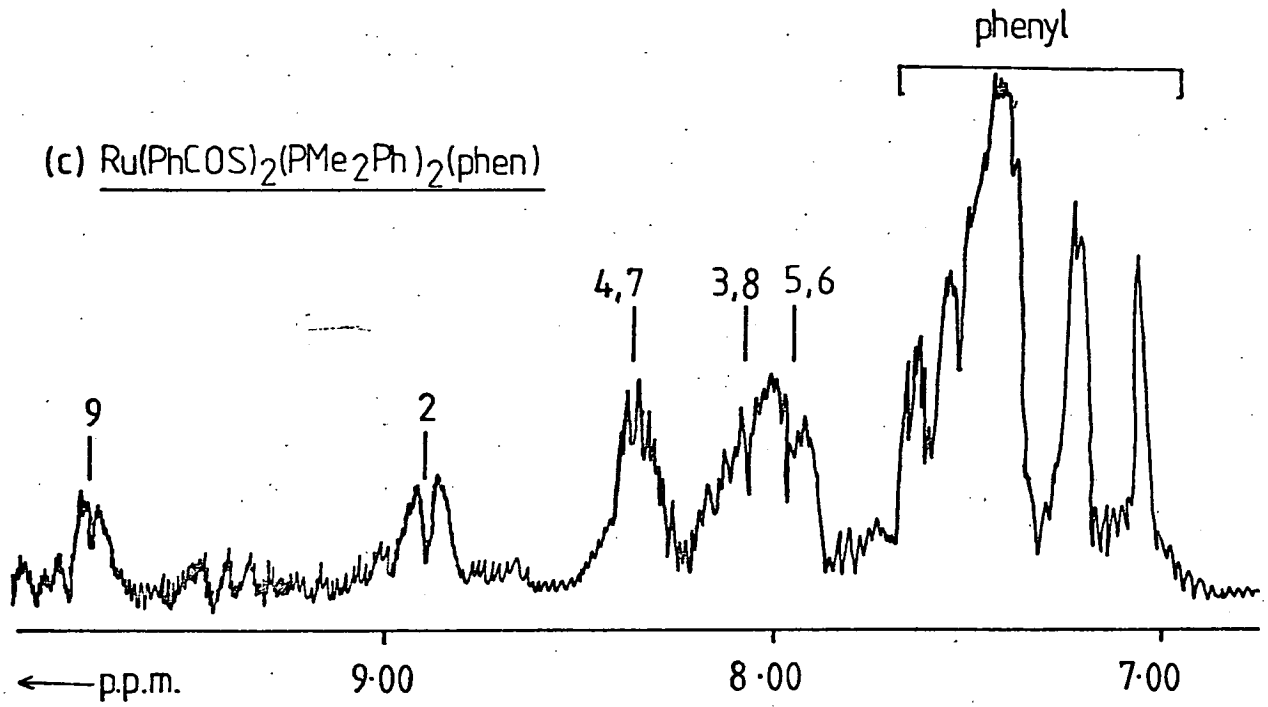
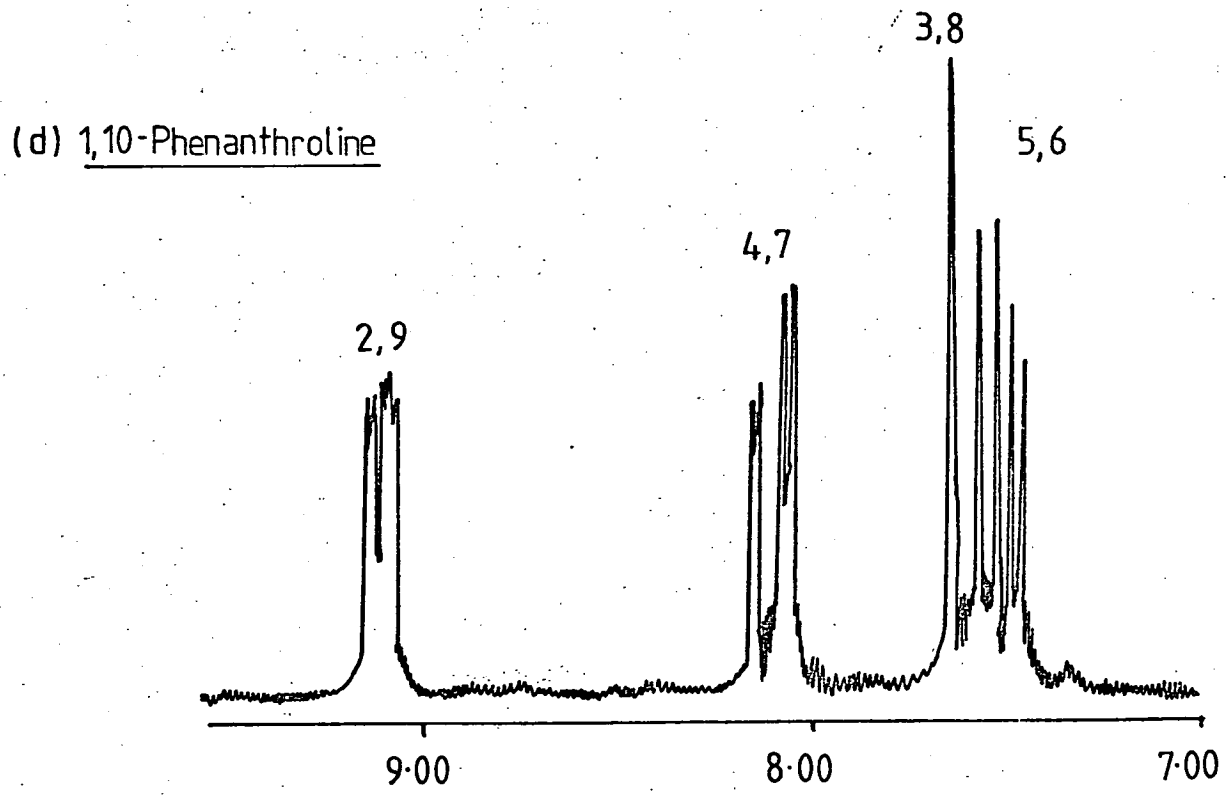
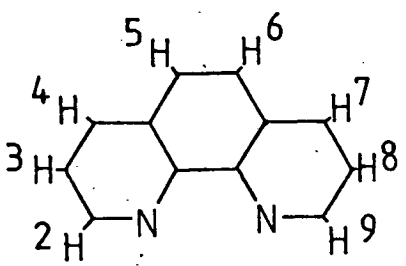
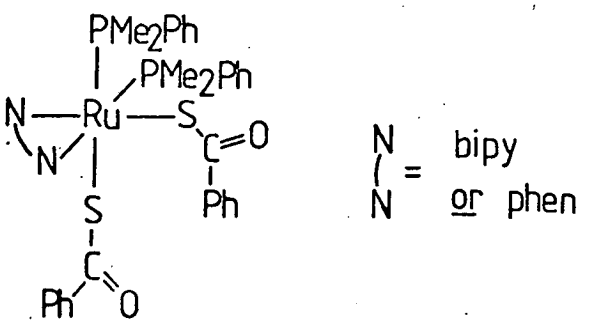


FIGURE 3.1 contd.









(29)

The apparent equivalence of the phosphines in the $^{31}P-\{^{1}H\}$-n.m.r. spectrum of $Ru(PhCOS)_2(PMe_2Ph)_2(bipy)$ must be ascribed to accidental coincidence of the chemical shifts of the phosphorus trans to sulphur and that trans to nitrogen. The inequivalence of the phosphine methyl groups and of the α-protons in the bipyridyl ligand give ample evidence that the anticipated structure containing cis-phosphines, both trans to nitrogen, is not present. A minor species of $Ru(PhCOS)_2(PMe_2Ph)_2(phen)$, containing trans-phosphines, gives rise to the triplet in the ^{1}H-n.m.r. and the singlet in the ^{31}P spectrum.

The cis-stereochemistry proposed above, and the coordination of the trans isomer have both been confirmed by X-ray structure determinations carried out on crystals of $Ru(PhCOS)_2(PMe_2Ph)_2(phen)$. The two isomers crystallised separately on the cooling of the reaction mixture, and examples of each suitable for data collection were selected and their structures solved.

3(iv) Determination of the Crystal Structures of cis, cis- and cis, trans-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$.

The ethanolic reaction mixture yielded dark red prismatic crystals, and preliminary precession and Weissenberg X-ray photographs revealed that two forms were present. Both were monoclinic, with cell dimensions as follows:

Form A	Form B
$a = 15.710(1)\text{Å}$	$a = 16.896(4)\text{Å}$
$b = 13.729(2)\text{Å}$	$b = 10.754(2)\text{Å}$
$c = 17.482(2)\text{Å}$	$c = 21.332(2)\text{Å}$
$\beta = 90.79(1)^{\circ}$	$\beta = 94.92(1)^{\circ}$

(These values were arrived at in each case by least-squares refinement based on twenty reflections selected and measured using a CAD-4 four-circle diffractometer, before data collection.)

The systematic absences observed in the preliminary photographs were the same in each case:

In the h 0 ℓ zone, $\ell = 2n + 1$ absent

Along the 0 k 0 row, $k = 2n + 1$ absent.

The space group was thus uniquely determined as $P2_1/c$ (n°. 14), which is centrosymmetric and has four equivalent positions in the unit cell. Assuming four molecules of formula $Ru(PhCOS)_2(PMe_2Ph)_2(phen)$ in each case, the calculated densities are 1.464 g cm^{-2} for form A and 1.430 g cm^{-2} for form B. The densities of different crystals from the same reaction mixture were measured as 1.451 g cm^{-2} and 1.423 g cm^{-2} by the flotation method, using water and saturated sodium bromide solution.

(a) Form A: cis, cis-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$

A crystal of $Ru(PhCOS)_2(PMe_2Ph)_2(phen)$, form A, was mounted in a random orientation on an ENRAF-Nonius CAD-4, four-circle automatic diffractometer. After refinement of the cell dimensions, three strong reflections were selected as intensity checks and data collection was

begun, using MoK_α radiation. Data were collected over one quarter of the molybdenum sphere (h k ℓ and h k $\bar{\ell}$ reflections) out to $\theta = 22^\circ$ and eventually 2782 observed reflections were used to solve the structure. After data reduction, including the application of Lorentz and polarisation factors, a Patterson summation was calculated and the position of the ruthenium atom was determined from the resulting vector map. The four equivalent positions in the unit cell are of the space group $P2_1/c$:

x, y, z

$-x, \frac{1}{2}+y, \frac{1}{2}-z$

$-x, -y, -z$

$x, \frac{1}{2}-y, \frac{1}{2}+z$

This results in a Patterson map containing ~~a Harker plane:~~ peaks $2x, \frac{1}{2}, 2z+\frac{1}{2}$, and ~~a Harker line:~~ $0, 2y+\frac{1}{2}, \frac{1}{2}$, both ~~containing two peaks~~ of weight two, together with a general point at 2x, 2y, 2z and the symmetry-related positions, of weight one. The peaks observed in the calculated Patterson map were identified as follows:

	$(2x, \frac{1}{2}, 2z+\frac{1}{2})$	at	(.4487, .5000, .6615)
	$(0, 2y-\frac{1}{2}, \frac{1}{2})$	at	(.0000, .0439, .5000)
	(2x, 2y, 2z)	at	(.4487, .4561, .1615)
giving	(x, y, z)	at	(.2244, .2280, .0808) .

The ruthenium atom was given this position in the calculation of subsequent Fourier maps, which were summed over that quarter of the unit cell bounded by all of a and c, and one quarter of b, to give one whole asymmetric unit. A difference Fourier map based on the ruthenium position revealed the sulphur and phosphorus atoms, and a series of a further four difference maps yielded positions for all the non-hydrogen atoms. Least-squares refinement of the structure, with the atomic

parameters for each ligand in a separate block of the matrix, was then begun, giving anisotropic temperature factors to the Ru, S and P atoms, and isotropic temperature factors to the C, O and N atoms. After two cycles, a further difference Fourier map was calculated in which peaks identifiable as hydrogen atoms were clearly visible. Ideal positions were calculated for all the hydrogen atoms and were used as a fixed contribution in further rounds of refinement. Unit weights were used throughout for all reflections and in the last cycle no parameter shifted by more than 0.4 times the standard deviation; the R-factor at convergence was 0.049.

(b) Form B: cis, trans-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$

A crystal of form B was mounted on a CAD-4 four-circle diffractometer and data were collected as described for form A, to give 2896 observed reflections which were used to solve the structure. After data reduction, a Patterson summation was calculated and the expected Harker peaks were picked out as follows:

	$(2x, \frac{1}{2}, 2z+\frac{1}{2})$	at	(.438, .5000, .5800)
	$(0, 2y+\frac{1}{2}, \frac{1}{2})$	at	(.0000, .0000, .5000)
	(2x, 2y, 2z)	at	(.437, .5000, .0810)
giving	(x, y, z)	at	(.2185, .2500, .0405) .

The value of $\frac{1}{4}$ found for y has two effects; firstly, it gives rise to pseudo-halving of the heavy-atom lattice along the b-axis, which means that there is no heavy-atom contribution to reflections with k = 2n+1, and these systematically weak reflections cannot be phased on the heavy atom position alone. Secondly, there is an ambiguity in the assignment of the peaks $(2x, \frac{1}{2}, 2z+\frac{1}{2})$ and $(2x, 2y, 2z+\frac{1}{2})$, so that there are two

possible non-equivalent solutions to the Patterson map, one giving (x, y, z) at (.2185, .2500, .0405) as above, and the other giving (x, y, z) at (.2185, .2500, .2905). The first solution was used in the initial attempts to solve the structure, and the ruthenium atom was given the position (.2185, .2500, .0405). In order to obtain phases for the systematically weak reflections, the direct methods programme DIRDIF.A[115] was used. This programme uses the triple product sign relationship to determine those phases in a centrosymmetric structure that cannot be determined from known heavy atom positions. The heavy atom contribution is subtracted from the observed structure factors for all reflections to which the heavy atoms contribute, to give the magnitude and sign of the light atom contribution. The structure factors for all reflections are then normalised to "E-values" for the difference or light atom structure; one reflection with $k = 2n+1$ is assigned a phase of 0 to fix the origin, and twenty others are assigned symbolic phases. The triple product sign relationship is then applied to all the light atom structure factors, the symbols are eliminated and the resulting set of phase reflections is used to calculate a Fourier map. When the DIRDIF.A procedure was applied in the present case, peaks assignable as two sulphur and two phosphorus atoms were located at reasonable bonding distances from the ruthenium, and a conventional difference Fourier map was calculated using the ruthenium, sulphur and phosphorus positions. In this map, fourteen atoms making up the 1,10-phenanthroline ligand were identified, all lying close to the $y = \frac{1}{4}$ plane. However, subsequent Fourier maps failed to reveal any further chemically meaningful structure and the alternative Patterson solution had to be considered. The second solution gives the heavy atom the coordinates (.2185, .2500, .2905), i.e. a shift

of $\frac{1}{4}$ along the c-axis from the first solution. This shift of $\frac{1}{4}$ in c was applied to the $RuS_2P_2(phen)$ fragment located using the first ruthenium position, and one difference Fourier map based on the new positions revealed all the remaining non-hydrogen atoms. Least-squares refinement was begun with the atoms of each ligand in a separate matrix block, and temperature factors anisotropic for Ru, S and P atoms, isotropic for C, O and N atoms. After two cycles, a difference Fourier map showed peaks identifiable as hydrogen atoms and these were placed in calculated ideal positions and applied as a fixed contribution to the structure in the subsequent refinement. Unit weights were used throughout, and on the last cycle no parameter shifted by more than 0.4 times the standard deviation. At convergence the R-factor was 0.061.

3(v) Discussion of the Structures

Structure factors and atomic positional and thermal parameters are given in Tables 3.4 - 3.6.

Bond lengths and angles for the two isomers are given in Table 3.3; the molecular structures and the crystal packing are shown in Diagrams 3.2 - 3.3.

The coordination about the ruthenium is in each case a distorted octahedron, with the narrow bite of the chelated 1, 10-phenanthroline ligand (N-Ru-N = 78.1° and 79.4°) producing the major distortions of angle. The Ru-P distances in the *cis*, *trans*- isomer, and the Ru-S distance *trans* to phosphorus in the *cis*, *cis*- case, are all significantly longer than the Ru-P and the Ru-S distances *trans* to nitrogen and sulphur, illustrating the *trans* influence of coordinated tertiary phosphines in metal complexes. The geometry of the unidentate monothiobenzoate groups is not significantly different in either case from

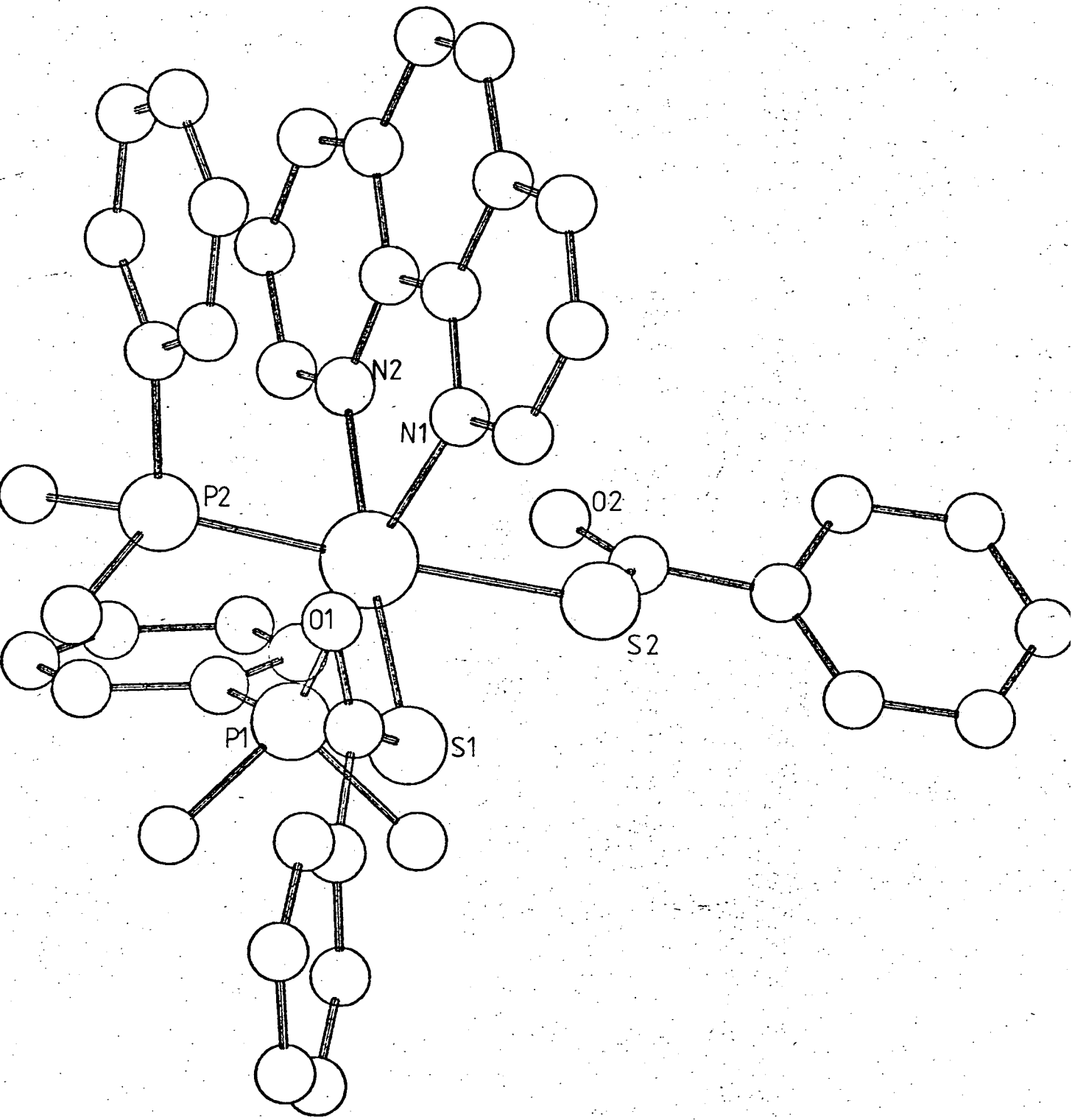


FIGURE 3.2 Molecular structure of

cis, cis - $Ru(PhCOS)_2(PMe_2Ph)_2(phen)$

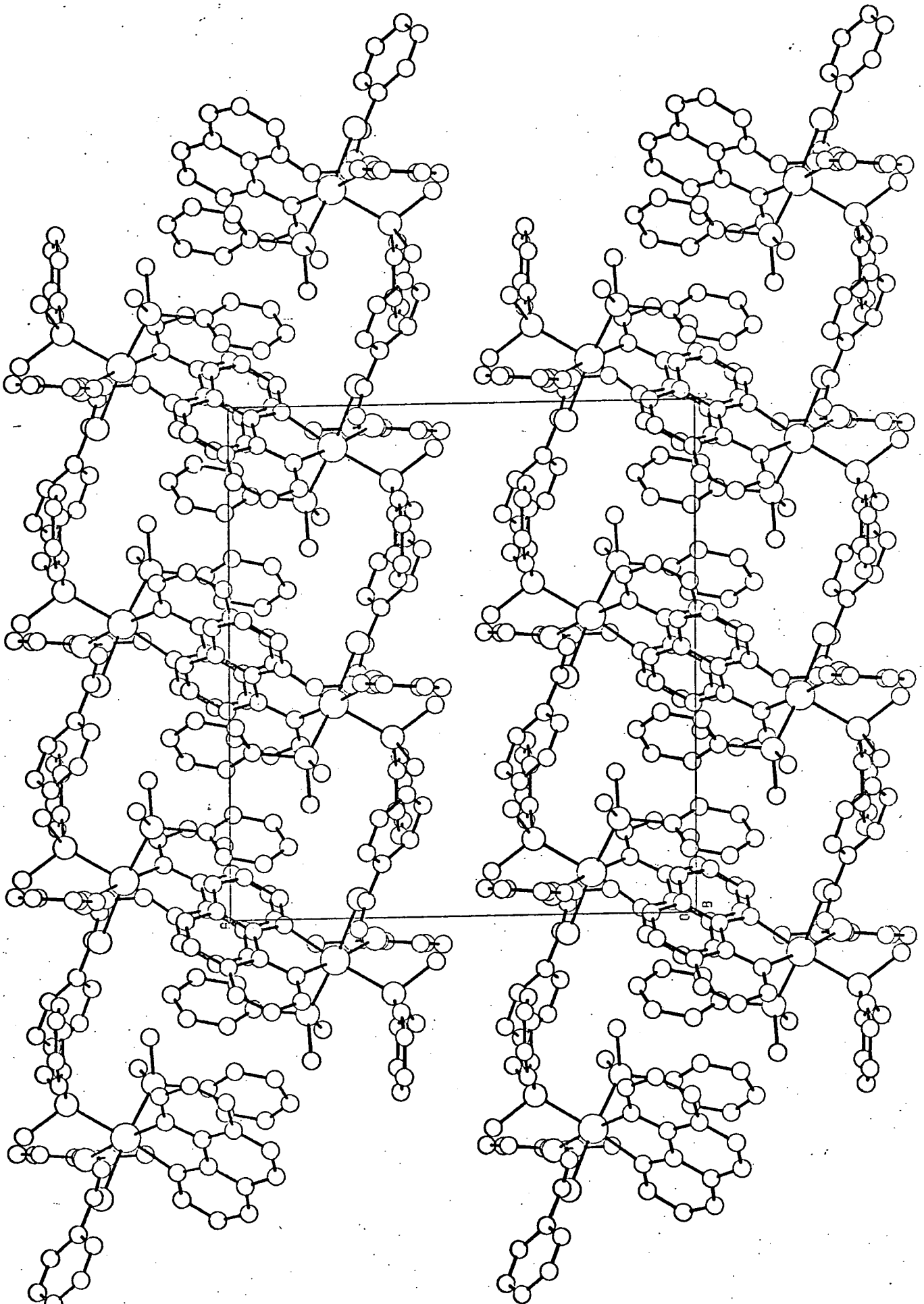


FIGURE 3.2. Crystal packing of cis,cis-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$

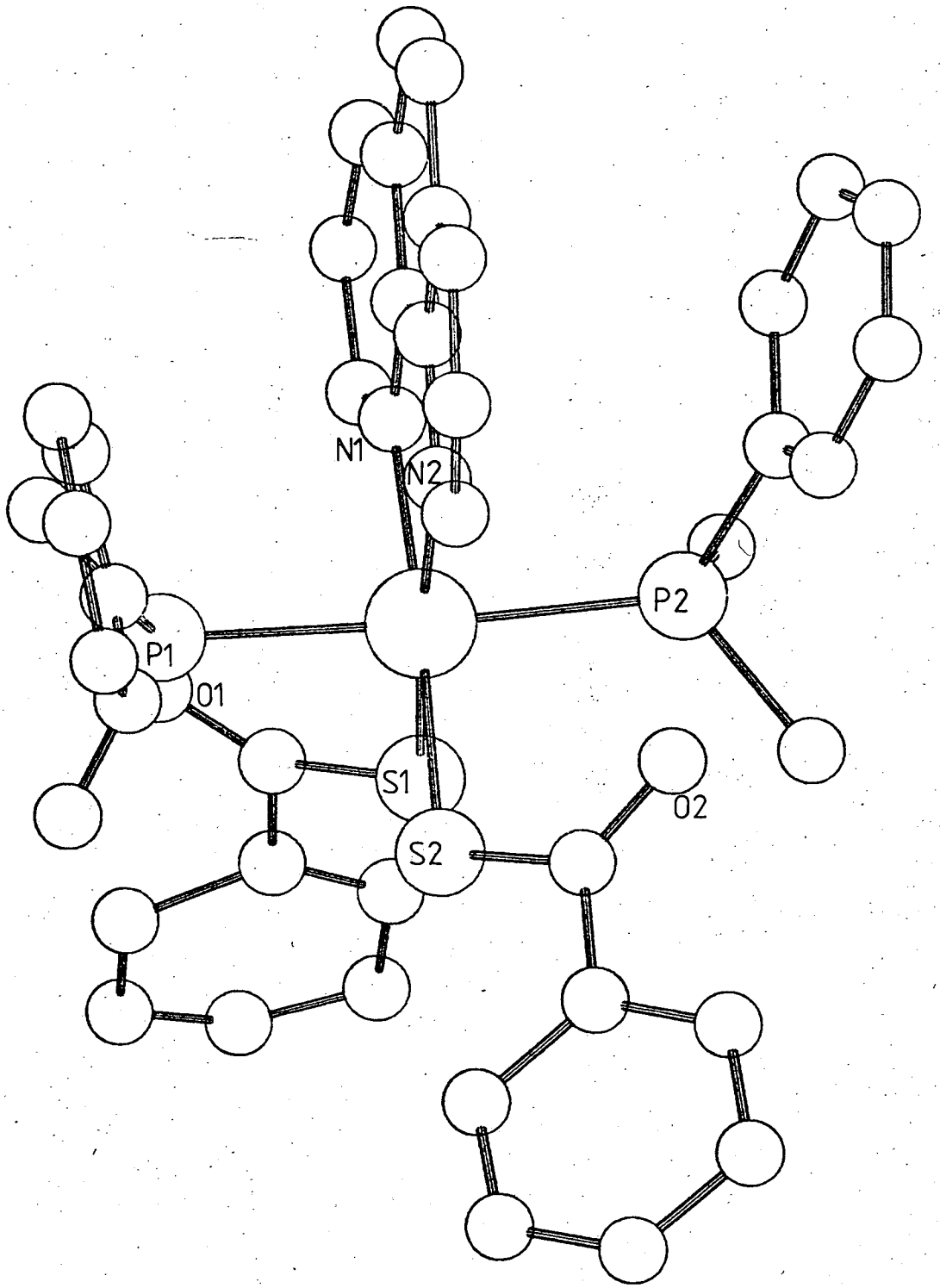


FIGURE 3.3 Molecular structure of cis,trans-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$

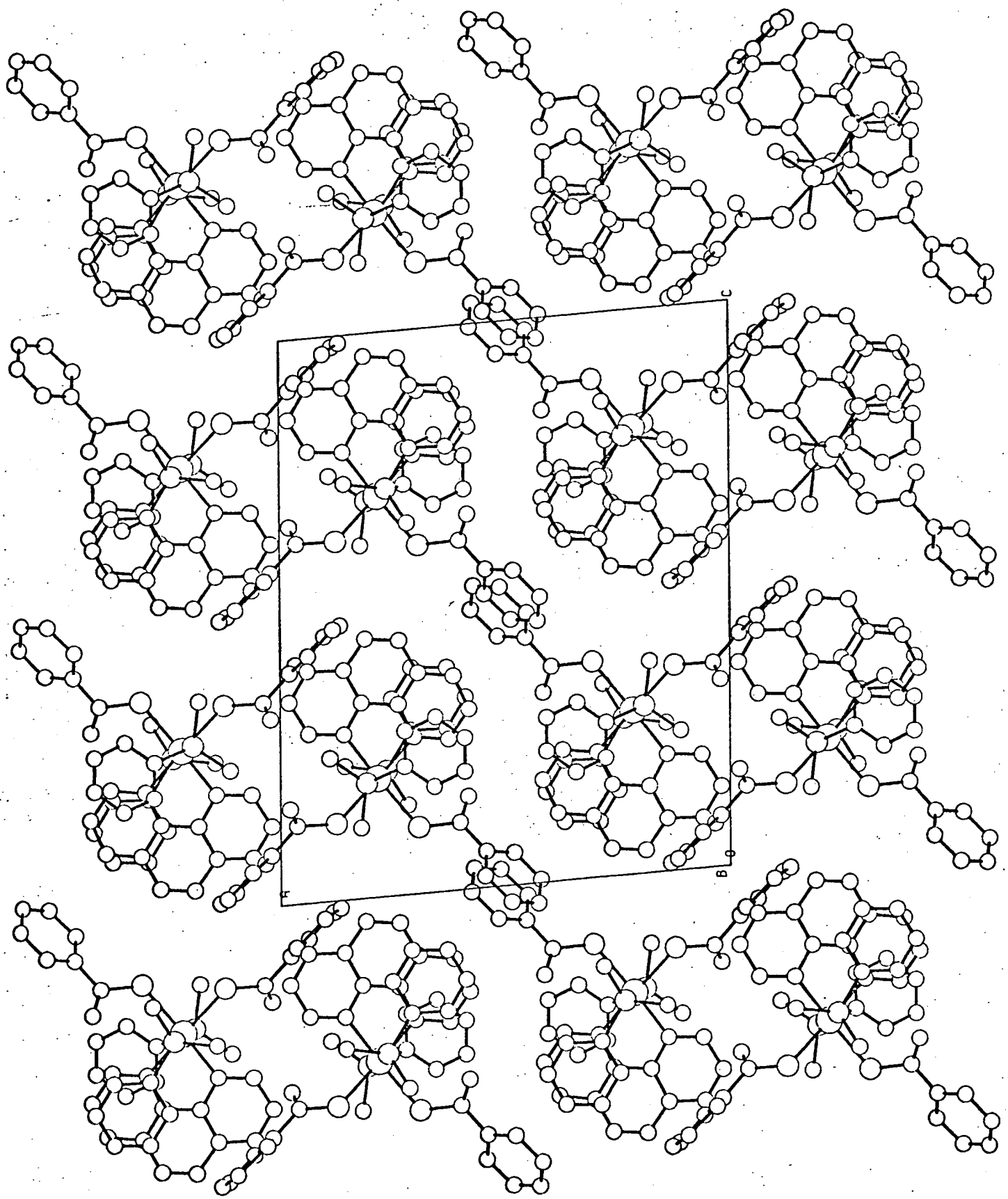


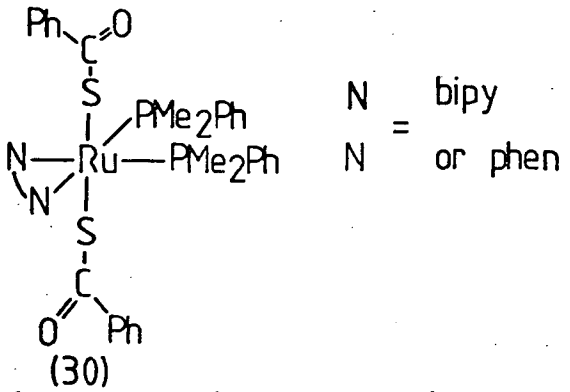
FIGURE 3.3 Crystal packing of cis,trans-$Ru(PhCOS)_2(PhCOS)_2(phen)$

that found in $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$ with Ru-S, S-C, O-C and C-Ph distances of ca 2.4 Å, 1.7 Å, 1.2 Å and 1.5 Å respectively, and the S-C-O angles ca 123°. Clearly, the sulphur has a fairly high mercaptide character in these complexes and the C-O bond has a high double-bond character, as would be expected. In the cis, cis- isomer, the monothiobenzoate group trans to nitrogen is twisted away from Ru-S-C-O planarity, with a Ru-S-C-O dihedral angle of -19.9°. This twist is apparently necessary to maximise the distance of the acid oxygen away from the cis atoms of the phenanthroline group, while keeping the monothiobenzoate phenyl ring clear of the substituents on the neighbouring phosphine. A similar phenomenon was noted in the structure of $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$, where hydrogen-bonding of the uncoordinated acid oxygen atoms to the coordinated amine nitrogen produced a Ru-S-C-O twist of 14° in one monothiobenzoate group. In the present case it illustrates the steric constraints which arise from the crowding of four phenyl-bearing ligands, together with the phenanthroline ring system, into the coordination sphere of a metal ion. Presumably it is this kind of constraint which determines the isomeric form of the $Ru(PhCOS)_2(PMe_2Ph)_2$ adducts formed with such a bulky Lewis base.

3(vi) Formation of cis, cis- and cis,trans-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$

The formation of cis,trans-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$ from the trans-phosphine isomer of $Ru(PhCOS)_2(PMe_2Ph)_2$ is possible by a simple Ru-O bond rupture mechanism without further rearrangement; thus, the minor isomer of the product is formed from the minor isomer of the starting material. Cis,cis-$Ru(PhCOS)_2(PMe_2Ph)_2(L_2)$, where

L_2 = bipy or phen, is presumably formed from the major cis-phosphine isomer of the starting material, but since simple rupture of the Ru-O bonds would give a product containing trans-monothiobenzoate groups and equivalent cis-phosphines (30), a rearrangement is clearly taking place. Examination of a molecular model of the trans-monothiobenzoate structure



(30)

shows that there are severe steric problems in accommodating two dimethylphenylphosphines in the same plane as a chelated 2,2'-bipyridyl or 1,10-phenanthroline ligand. The problem is less severe when one of the phosphines changes places with a monothiobenzoate group but even so, the acid group is twisted away from its preferred coordination geometry (see 3(v)). Thus it seems that the cis,cis isomer is more thermodynamically stable than the predicted isomer (30) and it is probably produced by rearrangement of an initial product formed from the cis-phosphine isomer of $Ru(PhCOS)_2(PMe_2Ph)_2$.

Experimental

Experimental details were as given in the Experimental section of Chapter 2. 2,2'-Bipyridyl and 1,10-phenanthroline hydrate were obtained from B.D.H.

Bis(dimethylphenylphosphine)(ethylenediammine)bis(monothiobenzoato)-ruthenium(II)

The compound $[Ru(PhCOS)_2(PMe_2Ph)_2]$ (0.10g) was refluxed in ethanol (50 ml) with ethylenediammine (0.10 ml) for 1h. The volume of the solution was reduced, and the yellow-brown microcrystalline product was filtered off (0.08g, 73%), m.p. 238-240°C. (Found: C, 53.38; H, 5.72; N, 4.01. Calc. for $C_{32}H_{40}N_2O_2P_2RuS_2$: C, 53.92; H, 5.62; N, 3.93%). Mull i.r. spectrum: $\nu_{(CS)}$ 930 cm^{-1} and $\nu_{(CO)}$ 1515 cm^{-1}.

(2,2'-Bipyridyl)bis(dimethylphenylphosphine)bis(monothiobenzoato)-ruthenium(II)

The compound $[Ru(PhCOS)_2(PMe_2Ph)_2]$ (0.07g) was refluxed in ethanol (30 ml) with 2,2'-bipyridyl (0.05g) for 2h. The volume of the solution was reduced and after standing for some hours the dark red crystalline product was filtered off (0.07g, 82%), m.p. 182-185°C (Found: C, 59.36; H, 5.01; N, 3.53. Calc. for $C_{40}H_{40}N_2O_2P_2RuS_2$: C, 59.48; H, 4.96; N, 3.47%). Mull i.r. spectrum: $\nu_{(CS)}$ 925 cm^{-1} and $\nu_{(CO)}$ 1550 cm^{-1}.

Bis(dimethylphenylphosphine)bis(monothiobenzoato)(1,10-phenanthroline)-ruthenium(II)

The compound $[Ru(PhCOS)_2(PMe_2Ph)_2]$ (0.05g) was refluxed in ethanol with 1,10-phenanthroline hydrate (0.05g) for 2h. The volume of the solution was reduced, and after standing for some hours, the dark red crystalline product was filtered off (0.06g, 94%), m.p. 216-218°C (Found: C, 60.43; H, 4.85; N, 3.49. Calc. for $C_{42}H_{42}N_2O_2P_2RuS_2$: C, 60.45; H, 4.81; N, 3.37%) Mull i.r. spectrum: $\nu_{(CS)}$ 927 cm^{-1} and $\nu_{(CO)}$ 1550 cm^{-1}.

TABLE 3.1

^{1}H-n.m.r. data in $CDCl_3$ for some ruthenium(II) monothiobenzoate complexes with bidentate nitrogen-donor Lewis bases (all at 300K).

Complex	δ ± 0.01 p.p.m. methyl of phosphine	other
$Ru(PhCOS)_2(PMe_2Ph)_2(en)$	1.69 (pt)	7.00 - 7.60[a]
$Ru(PhCOS)_2(PMe_2Ph)_2(bipy)$	1.37 (d)	7.00 - 7.50[a]
	1.38(d)	7.76(m)[b]
	1.98 (d)	8.02(m)[b]
	2.04 (d)	8.32(m)[b]
		8.56(d)[b]
		9.50(d)[b]
$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$	1.25 (d)	7.00 - 7.50[a]
	1.34 (d)	7.96(m)[c]
	1.50 (t)	8.05(m)[c]
	2.06 (d)	8.37(m)[c]
	2.14 (d)	8.89(m)[c]
		9.75(m)[c]

pt = pseudo-triplet d = doublet t = triplet m = multiplet

[a] phenyl resonances

[b] 3 and 3', 4 and 4', 5 and 5', 2, and 2' protons of bipy

[c] 5 and 6, 3 and 8, 4 and 7, 2, and 9 protons of phen

See Diagram 3.1 a - d.

TABLE 3.2

$^{31}P-\{^{1}H\}$-n.m.r. data in $CDCl_3$ for some ruthenium(II) monothiobenzoate complexes with bidentate nitrogen-donor Lewis bases

Complex	T/K	δ ± 0.01 p.p.m.[a]	δ(PP)/Hz	J(PP)Hz
$Ru(PhCOS)_2(PMe_2Ph)_2(en)$	300	21.72 (s)		
$Ru(PhCOS)_2(PMe_2Ph)_2(bipy)$	300	14.05 (s)		
	223	15.28 (s)		
$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$	300	5.73 (s)		
		12.87 (ab)	47.5	30.8
	233	12.60 (ab)	88.1	31.4

ab = AB pattern; parameters obtained by refinement using LAOCOON program

a ^{31}P chemical shifts quoted in p.p.m. to high frequency of 85% H_3PO_4.

TABLE 3.3

Interatomic distances and angles for cis,cis-$Ru(PhCOS)_2(PMe_2Ph)(phen)$ and cis-trans-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$

Estimated standard deviations are given in brackets.

Interatomic distances (Å)

	cis,cis-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$	cis,trans-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$
Ru-P1	2.346(2)	2.380(3)
Ru-P2	2.333(2)	2.365(3)
Ru-S1	2.399(2)	2.404(3)
Ru-S2	2.450(3)	2.398(2)
Ru-N1	2.122(7)	2.082(7)
Ru-N2	2.114(8)	2.091(8)
P1-C1	1.836(11)	1.823(13)
P1-C2	1.819(11)	1.819(13)
P1-C3	1.848(10)	1.833(12)
P2-C9	1.820(11)	1.827(13)
P2-C10	1.813(10)	1.818(12)
P2-C11	1.832(9)	1.840(12)
S1-C17	1.744(9)	1.712(12)
C17-O1	1.244(12)	1.22(2)
C17-C18	1.505(13)	1.52(2)
S2-C24	1.743(9)	1.717(11)
C24-O2	1.219(11)	1.24(1)
C24-C25	1.506(12)	1.49(1)
av. C-C(phenyl)	1.382	1.37
σ(mean)	0.019	0.06
mean σ	0.015	0.02

Interatomic angles (°)

P1-Ru-P2	94.10(4)	176.8(4)
P1-Ru-S1	82.81(9)	84.4(1)
P1-Ru-S2	91.84(9)	96.5(1)
P1-Ru-N1	173.7(2)	86.9(3)

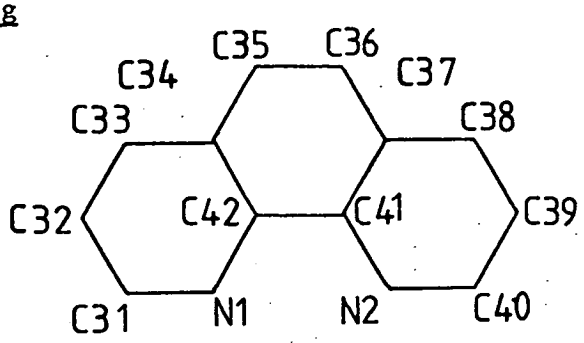
TABLE 3.3 (Contd.)

Interatomic angles (^{o})

	cis,cis-$Ru(PhCOS)_2(PMe_2Ph)_2$(phen)	cis,trans-$Ru(PhCOS)_2(PMe_2Ph)_2$(phe
P1-Ru-N2	102.0(2)	91.1(2)
P2-Ru-S1	95.52(8)	96.0(1)
P2-Ru-S2	173.4(2)	86.6(1)
P2-Ru-N1	92.2(2)	90.0(3)
P2-Ru-N2	85.3(2)	88.3(2)
S1-Ru-S2	82.22(9)	83.8(1)
S1-Ru-N1	97.0(2)	98.9(2)
S1-Ru-N2	175.0(4)	175.4(4)
S2-Ru-N1	81.9(2)	175.8(4)
S2-Ru-N2	96.4(2)	98.1(2)
N1-Ru-N2	78.1(3)	79.4(3)
Ru-P1-C1	114.0(3)	113.4(4)
Ru-P1-C2	116.2(4)	121.1(4)
Ru-P1-C3	123.8(3)	113.9(4)
C1-P1-C2	98.5(5)	98.9(6)
C1-P1-C3	99.3(4)	102.3(5)
C2-P1-C3	101.1(5)	104.7(5)
Ru-P2-C9	123.8(4)	117.8(4)
Ru-P2-C10	115.8(3)	117.6(4)
Ru-P2-C11	111.6(3)	111.6(4)
C9-P2-C10	99.2(5)	103.8(6)
C9-P2-C11	102.2(4)	102.6(5)
C10-P2-C11	101.3(4)	101.2(5)
Ru-S1-C17	115.8(3)	116.9(4)
S1-C17-O1	124.1(7)	125.5(10)
S1-C17-C18	117.0(7)	116.3(9)
O1-C17-C18	118.8(8)	118.0(11)
Ru-S2-C24	114.9(3)	116.1(4)
S2-C24-O2	124.6(7)	124.1(8)
S2-C24-C25	115.3(6)	118.2(8)
O2-C24-C25	120.0(8)	117.7(9)
av. C-C-C (phenyl)	119.9	119.9
σ(mean)	1.3	4.0
mean σ	1.4	1.4

TABLE 3.3 (Contd.)

1,10-phenthroline ring



Interatomic distances (Å)

	cis,cis-Ru(PhCOS)$_2$(PMe$_2$Ph)$_2$(phen)	cis,trans-Ru(PhCOS)$_2$(PMe$_2$Ph)$_2$(phen
N1-C31	1.33(1)	1.33(1)
C31-C32	1.41(1)	1.41(2)
C32-C33	1.37(2)	1.36(2)
C33-C34	1.40(1)	1.38(2)
C34-C35	1.44(1)	1.44(2)
C35-C36	1.32(1)	1.30(2)
C36-C37	1.44(1)	1.41(2)
C37-C38	1.38(1)	1.40(2)
C38-C39	1.34(2)	1.36(1)
C39-C40	1.39(1)	1.39(2)
C40-N2	1.34(1)	1.32(1)
N2-C41	1.36(1)	1.36(1)
C41-C37	1.41(1)	1.42(1)
C41-C42	1.41(1)	1.42(1)
C42-C34	1.43(1)	1.42(1)
C42-N1	1.37(1)	1.38(1)

Interatomic angles (°)

Ru-N1-C31	128.2(6)	128.7(7)
N1-C31-C32	122.4(8)	122(1)
C31-C32-C33	119.5(9)	119(1)
C32-C33-C34	120(1)	122(1)
C33-C34-C42	117.2(9)	116(1)

TABLE 3.3 (Contd.)

Interatomic Angles (°)

	cis,cis-$Ru(PhCOS)_2PMe_2Ph)_2$(phen)	cis,trans-$Ru(PhCOS)_2(PMe_2Ph)_2$(phen)
C42-C34-C35	117.7(9)	116(1)
C34-C35-C36	120(1)	122(1)
C35-C36-C37	122(1)	123(1)
C36-C37-C41	118.7(9)	118(1)
C41-C37-C38	116.6(9)	116(1)
C37-C38-C39	121(1)	120(1)
C38-C39-C40	119(1)	120(1)
C39-C40-N2	123.2(9)	123(1)
C40-N2-Ru	129.4(6)	129.4(6)
C40-N2-C41	116.5(8)	117(1)
C41-N2-Ru	114.0(6)	113.6(6)
N2-C41-C37	123.3(8)	124(1)
C37-C41-C42	119.5(8)	119(1)
N2-C41-C42	117.1(8)	117(1)
C41-C42-N1	117.6(8)	117(1)
C41-C42-C34	120.4(8)	121(1)
C34-C41-N1	120.0(8)	122(1)
C41-N1-Ru	113.2(5)	113.1(6)
C41-N1-C31	118.6(7)	118(1)

TABLE 3.4

Positional and thermal parameters ($\times 10^4$) for the atoms of cis, cis-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$

Atom	x/a	y/b	z/c	U/A^2
Ru	2237.7(5)	2275.7(6)	815.4(4)	a
N1	1161(4)	2572(5)	108(4)	255(18)
N2	1408(4)	1124(6)	1104(4)	275(18)
C31	1066(5)	3272(7)	-415(5)	301(23)
C32	305(7)	3401(8)	-836(6)	389(26)
C33	-367(6)	2785(8)	-716(6)	425(25)
C34	-291(6)	2026(7)	-185(6)	356(25)
C35	-955(7)	1350(8)	-1(6)	439(28)
C36	1839(7)	644(8)	503(6)	438(28)
C37	-45(6)	529(7)	912(6)	340(24)
C38	115(7)	-181(8)	1458(6)	434(28)
C39	882(7)	-255(8)	1802(6)	416(27)
C40	1524(6)	397(7)	1605(6)	350(24)
C41	630(6)	1176(7)	752(5)	285(22)
C42	510(6)	1940(7)	222(5)	298(23)
P2	1646(2)	3089(2)	1852(1)	a
C9	1968(7)	4301(8)	2161(6)	422(26)
C10	1719(6)	2462(8)	2764(6)	429(27)
C11	491(6)	3225(7)	1737(5)	291(22)
C12	-76(6)	2553(7)	2055(5)	347(24)
C13	-939(6)	2591(8)	1892(6)	419(26)
C14	-1263(7)	3295(8)	1416(6)	460(28)
C15	-73(7)	3961(8)	1092(6)	451(27)
C16	134(6)	3943(7)	1247(6)	338(23)
S1	3091(2)	3620(2)	402(1)	a
C17	2612(6)	4765(7)	449(5)	281(22)
O1	1831(4)	4898(5)	479(4)	451(18)
C18	3193(6)	5637(7)	442(5)	306(22)
C19	2824(7)	6544(8)	417(6)	467(28)
C20	3315(7)	7384(9)	452(7)	576(32)
C21	4181(7)	7309(9)	510(6)	545(29)
C22	4544(7)	6437(8)	533(6)	485(29)

TABLE 3.4 (Contd.)

Atom	x/a	y/b	z/c	U/A^2
C23	4066(6)	5568(8)	515(6)	383(25)
S2	2760(2)	1547(2)	-369(1)	[a]
C24	2914(5)	291(6)	-333(5)	247(21)
O2	2740(4)	-221(5)	217(4)	370(16)
C25	3251(6)	-161(7)	-1053(5)	262(22)
C26	2928(6)	-106(7)	-1273(5)	330(23)
C27	3200(7)	-1514(8)	-1904(6)	464(28)
C28	3787(7)	-1062(8)	-2392(6)	436(27)
C29	4131(7)	-184(8)	-2174(6)	560(28)
C30	3851(6)	277(7)	-1513(5)	315(23)
P1	3487(2)	1849(2)	1485(1)	[a]
C1	4398(7)	1600(8)	867(6)	413(26)
C2	3966(6)	2799(9)	2075(6)	446(26)
C3	3574(6)	788(7)	2132(5)	314(23)
C4	3644(7)	-134(8)	1849(6)	415(26)
C5	3711(7)	-945(8)	2334(6)	485(29)
C6	3702(7)	-817(9)	3115(7)	541(31)
C7	3622(8)	92(9)	3402(7)	586(33)
C8	3556(6)	906(8)	2927(6)	377(25)

Anisotropic temperature factors $(\times 10^4)/A^{o2}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	276(4)	233(4)	259(4)	-15(4)	23(3)	4(4)
P2	257(12)	296(14)	243(13)	-15(11)	19(9)	30(11)
S1	276(13)	196(13)	452(16)	-1(10)	76(11)	-57(11)
S2	450(15)	237(13)	259(13)	65(11)	76(11)	7(11)
P1	258(13)	272(13)	310(14)	-15(11)	-12(11)	31(12)

[a] anisotropic temperature factor.

TABLE 3.4 (Contd.)

Calculated hydrogen atom positions ($U = 0.05 A^2$ (fixed))

Atom	x/a	y/b	z/c
H101	4247	1052	509
H102	4519	2199	552
H103	4936	1419	1145
H201	4105	3365	1721
H202	3540	3018	2449
H203	4502	2625	2351
H4	6316	243	8719
H5	6253	1631	7889
H6	6225	1402	6540
H7	6362	183	3974
H8	6591	1602	3140
H12	161	2019	2410
H13	1342	2083	2126
H14	-1909	3328	1299
H15	-962	4477	1729
H16	523	4448	1015
H19	2187	1601	0363
H20	3041	8056	0442
H21	4537	7923	0556
H23	4359	5091	0555
H26	2510	1394	930
H27	2963	-2163	-2083
H28	3963	-1380	-2897
H29	4602	-135	-2494
H30	5920	-954	-1385
H31	1563	3725	509
H32	254	3926	1241
H33	-923	2882	-1008
H35	-1529	1421	-278
H36	-1328	176	622
H38	-367	-622	1620
H39	1003	-778	2204
H40	2122	312	1870
H901	1602	4807	3087
H902	2581	4425	2984
H903	1920	4340	2270
H1001	2324	2209	2256
H1002	1324	1897	2336
H1003	1668	2518	8342

TABLE 3.5

Positional and thermal parameters ($\times 10^4$) for the atoms of *cis,trans*-$Ru(PhCOS)_2(PMe_2Ph)_2(phen)$

Atom	x/a	y/b	z/c	U/A^{o_2}
Ru	2163.6(5)	2562.4(9)	2897.6(3)	a
N1	1409(4)	2481(9)	2074(4)	405
N2	2963(4)	2950(7)	2227(4)	325
C31	629(6)	2307(11)	2009(5)	519
C32	194(7)	2263(12)	1416(6)	675
C33	590(7)	2397(14)	892(6)	716
C34	1399(6)	2601(12)	924(5)	515
C35	1883(7)	2774(12)	406(5)	584
C36	2643(7)	3012(12)	488(6)	600
C37	3054(6)	3127(10)	1089(5)	444
C38	3854(6)	3437(11)	1208(5)	464
C39	4180(6)	3513(10)	1813(5)	441
C40	3724(6)	3256(10)	2310(5)	402
C41	2629(6)	2902(9)	1622(4)	368
C42	1800(6)	2655(10)	1537(4)	393
P2	1925(2)	4722(3)	2967(1)	a
C9	1792(7)	5371(12)	3743(6)	651
C10	1101(7)	5365(12)	2467(6)	598
C11	2762(6)	5637(10)	2716(5)	472
C12	3421(7)	5838(11)	3128(5)	534
C13	4082(8)	6437(13)	2913(6)	666
C14	4093(8)	6778(12)	2304(6)	671
C15	3431(8)	6608(12)	1898(6)	640
C16	2765(7)	6036(11)	2103(6)	542
S1	1238(2)	1948(3)	3635(1)	a
C17	372(7)	2778(11)	3626(5)	553
O1	210(6)	3702(10)	3308(5)	958
C18	-219(7)	2363(14)	4091(6)	675
C19	-626(10)	3397(17)	4362(8)	1055
C20	-1223(13)	2957(22)	4804(10)	1304
C21	-1299(14)	1805(25)	4853(11)	1377
C22	-921(14)	871(23)	4702(11)	1427
C23	-310(10)	1207(17)	4245(8)	975

TABLE 3.5 (Contd.)

Atom	x/a	y/b	z/c	U/A^{o2}
C24	3971(6)	2092(10)	3806(5)	446
O2	4168(4)	1447(8)	3360(4)	559
C25	4562(6)	2247(10)	4361(4)	392
C26	4535(6)	3199(10)	4804(5)	452
C27	5121(7)	3281(11)	5299(5)	513
C28	5718(6)	2456(13)	5360(5)	581
C29	5763(8)	1508(14)	4941(7)	782
C30	5184(7)	1423(12)	4435(6)	594
P1	2355(2)	386(3)	2776(1)	[a]
C1	1428(7)	-478(12)	2637(6)	631
C2	2826(8)	-548(13)	3413(6)	668
C3	2879(6)	- 27(10)	2087(5)	453
C4	3697(6)	-34(11)	2122(5)	507
C5	4096(7)	-295(12)	1589(6)	633
C6	3683(8)	-467(13)	1037(6)	664
C7	2900(9)	-435(14)	979(7)	836
C8	2466(8)	-217(12)	1510(6)	658

Anisotropic temperature factors ($\times 10^4$)/A^{o2}

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	360	473	273	-18	48	2
P2	391	463	422	60	48	-55
S1	426	725	340	-28	119	64
S2	398	585	269	43	20	-18
P1	531	399	426	-62	105	11

Calculated hydrogen atom positions (U = 0.05A^{o2}, fixed)

Atom	x/a	y/b	z/c
H101	1520	-1353	2503
H102	1116	-478	3014
H103	1170	37	2286
H201	2511	-548	3790
H202	2916	-1423	3280
H203	3333	-73	3490
H4	4010	139	2534
H5	4691	-340	1622

TABLE 3.5 (Contd.)

Atom	x/a	y/b	z/c
H6	3974	-638	656
H7	2603	-562	557
H8	1875	193	1462
H12	3432	5566	3579
H13	4559	6614	3212
H14	4583	7154	2148
H15	3437	6898	1452
H16	2282	5926	1803
H19	-535	4293	4250
H20	-1501	3612	5062
H21	-1802	1632	5036
H22	-983	31	4886
H23	13	561	4064
H26	4095	3825	4762
H27	5098	3966	5616
H28	6133	2523	5722
H29	6213	905	4986
H30	5221	728	4123
H31	335	2205	2394
H32	-395	2124	1381
H33	285	2362	470
H35	1626	2736	-37
H36	2948	3099	110
H38	4184	3607	852
H39	4751	3765	1898
H40	3994	3269	2748
H901	1822	6295	3737
H902	1278	5099	3894
H903	2251	5013	4018
H1001	582	5095	2619
H1002	1126	6292	2462
H1003	1172	5010	2044

Table 3.6a: Structure factors for cis,cis-Ru(PhCOS)$_2$(PMe$_2$Ph)$_2$(phen)
Columns are l, 10|F_o|, 10|F_c|.

0,0,L

2	2128	2110
4	379	325
6	483	535
8	1924	1972
10	501	549
12	694	669

0,1,L

1	674	665
2	3080	3120
3	734	709
4	962	907
6	672	619
7	477	513
8	1153	1226
9	634	658
10	1106	1171
11	318	335
12	233	247
13	528	572
14	480	507
16	760	855
17	267	291

0,2,L

0	1368	1525
1	424	443
2	1000	973
3	1250	1293
5	518	554
6	918	969
7	1080	1059
8	812	812
9	714	721
10	612	603
11	623	630
12	874	901
14	569	548
15	594	554
18	646	711

0,3,L

2	441	472
3	1094	1087
5	867	920
6	411	464
10	867	947
13	627	618
14	574	567
16	751	744
17	295	379

0,4,L

0	1324	1363
1	301	334
3	992	991
4	213	206
5	186	243
6	251	330
7	653	657
8	847	853
10	464	476
11	560	602
12	976	962
14	600	604
15	759	735

0,5,L

1	981	957
2	342	339
4	956	1049
5	520	561
6	525	562
8	1083	1065
10	491	496
13	475	505
16	384	390
17	635	648

0,6,L

0	284	284
2	534	536
3	1479	1458
5	803	800
6	1597	1557
7	439	410
10	879	884
11	499	555
12	451	451
14	727	699
15	508	523

0,7,L

1	625	668
2	533	537
3	538	516
4	1140	1187
5	1094	1132
7	425	478
8	320	307
12	250	245
13	737	694
16	255	241

0,8,L

0	752	725
1	466	505
2	752	753
3	1310	1294
5	908	931
6	750	750
7	337	287
11	294	298
15	428	361

0,9,L

1	590	597
2	282	282
4	690	745
5	721	728
7	676	664
8	576	584
11	654	624
13	507	539

0,10,L

0	287	275
1	275	331
2	857	838
3	509	520
4	427	443
5	278	213
6	273	260
7	741	743
8	364	385
9	1052	1079
11	427	437
13	365	329

0,11,L

1	363	443
2	249	261
3	276	210
4	510	448
5	545	530
7	611	579
11	887	877

0,12,L

0	229	177
1	472	393
2	263	238
3	648	699
5	394	352
9	893	901

0,13,L

5	368	386
6	324	310
7	615	620

0,14,L

1	249	196
2	452	455
3	291	312
4	322	286

1,0,L

-16	789	761
-14	490	507
-12	485	483
-10	312	299
-8	1446	1431
-6	1312	1235
-4	3478	3344
-2	495	4118
0	1496	1455
2	2752	2702
4	1095	1106
6	254	299
8	1852	1929
10	638	675
12	479	471
14	319	271

1,1,L

-18	790	787
-16	442	445
-15	515	562
-14	428	429
-13	260	295
-12	316	367
-10	438	429
-9	1071	1044
-8	953	915
-7	751	773
-6	1237	1218
-5	1423	1357
-4	524	538
-1	474	474
0	3172	3078
1	328	359
2	1473	1477
3	1493	1449
4	324	314
5	1588	1551
6	408	473
7	666	722
8	875	858

1,1,L

11	380	382
12	927	951
13	265	277
15	533	504
16	541	563
18	396	445

1,2,L

-17	360	334
-16	759	754
-14	620	628
-10	572	559
-8	1065	987
-7	276	237
-6	327	295
-5	1896	1841
-4	1922	1828
-2	1380	1365
-1	1470	1433
0	1341	1314
2	1850	1872
3	608	592
4	342	423
5	411	445
6	771	704
8	636	719
9	386	391
10	1520	1578
12	318	246
13	452	482
14	571	579
16	631	600
17	391	427

1,3,L

-15	679	667
-14	465	419
-13	326	323
-12	777	788
-11	690	701
-10	764	691
-8	294	298
-7	1515	1462
-6	1337	1317
-5	563	555
-3	2395	2322
-2	787	741
-1	261	267
0	1634	1654
1	278	334
2	263	146
3	408	371
4	1072	1070

1,4,L

-17	294	357
-16	538	499
-14	406	356
-13	221	283
-11	313	391
-10	698	742
-8	673	697
-6	458	475
-5	1741	1727
-4	1676	1615
-3	285	321
-2	964	1018
-1	1235	1211
0	562	558
1	762	807
2	1410	1407
3	225	249
4	456	574
6	432	424
7	538	564
10	639	673
13	399	430
16	588	565
17	575	525

1,5,L

-15	619	628
-14	718	724
-12	865	846
-11	754	729
-10	815	773
-9	471	418
-6	1064	1100
-5	226	179
-4	1161	1153
-3	1193	1188
-2	1140	1092
-1	311	197
0	283	380
1	567	530
3	673	676
4	713	170
6	475	531
7	494	538

1,6,L

-14	521	540
-13	653	702
-8	568	579
-6	190	173
-5	958	1030
-4	686	743
-2	618	612
-1	876	892
0	409	449
1	755	723
2	238	280
3	225	254
4	1428	1435
5	597	656
6	214	238
7	791	748
8	770	775
9	382	386
10	385	378
13	708	732
14	259	242
16	377	401

1,7,L

-15	337	312
-12	437	421
-10	525	519
-9	234	188
-6	665	685
-5	831	585
-4	272	281
-3	1400	1463
-1	825	829
1	296	317
2	893	796
3	1059	1092
5	1069	1157
6	1090	1101
7	349	324
8	340	354
9	311	239
10	717	717
12	326	300
14	402	406
15	479	461

1,8,L

-14	491	425
-13	460	443
-11	981	984
-7	623	651
-5	678	735
-4	1007	997
-1	745	716
1	1003	998
4	1419	1436
5	755	810
6	340	301
7	968	981
8	355	338
9	343	368
11	588	521
13	435	396

1,9,L

-13	437	503
-10	396	380
-9	849	826
-6	441	476
-5	646	656
-3	741	744
-2	698	768
-1	631	636
0	211	277
2	911	898
3	952	977
4	259	251
5	723	759
6	544	540
9	616	602
10	358	393
11	247	288

1,10,L

-13	503	519
-11	910	924
-7	725	789
-5	667	639
-4	360	358
-3	312	313
-2	446	481
1	496	516
2	374	319
4	334	350
5	842	845
7	748	769
11	580	561
13	500	504

1,11,L

-11	433	439
-9	1167	1160
-7	685	677
-3	279	280
-1	650	664
1	405	360
3	603	575
4	278	241
7	439	468
8	396	378
9	774	797
11	339	315

1,12,L

-7	698	726
-2	251	254
-1	478	422
1	1108	1052
2	319	286
3	256	232
5	567	526
6	253	255
7	837	801

1,13,L

-7	340	347
3	364	390
6	293	257
7	486	449

1,14,L

-4	292	332
-1	527	513
1	575	517
4	366	387

2,0,L

-18	971	997
-16	687	716
-14	543	530
-12	744	766
-10	455	443
-8	237	277
-4	1589	1446
-2	783	734
0	2202	2094
2	1713	1753
4	421	494
6	1067	1021
8	1359	1422
10	910	871
12	726	710
16	316	253

2,1,L

-16	870	905
-14	299	220
-10	806	814
-9	217	155
-8	1432	1400
-7	537	471
-6	926	892
-5	973	873
-4	1722	1581
-3	1310	1238
-2	1735	1604
0	1061	1064
1	231	223
2	1085	1091
3	1149	1096
4	715	725
6	376	416
9	711	694
10	1596	1547
12	650	612
14	685	655
16	300	320

2,2,L

-18	858	897
-16	410	347
-14	373	334
-11	269	178
-10	643	653
-7	1089	1044
-6	1401	1326
-5	2176	2052
-4	2289	2284
-3	864	745
-2	855	855
-1	320	316
0	554	602
1	694	678
2	1037	953
4	225	248
5	740	682
6	1018	1059
7	537	590
8	824	852
9	896	910
10	244	249
12	1273	1305
14	437	480
15	276	267
17	289	295

2,3,L

-16	470	422
-14	672	662
-13	367	385
-11	442	381
-10	734	702
-9	660	586
-8	1037	1009
-7	844	783
-5	2198	2064
-4	2284	2127
-3	1733	1510
-2	2390	2203
-1	919	871
0	252	291
1	699	696
4	1511	1481
5	573	566
7	461	448
8	374	417
10	1127	1080
11	255	218
13	233	221
14	415	469
16	593	603
17	270	267

2,4,L

-15	668	656
-12	1111	1093
-11	447	420
-10	599	627
-9	484	468
-8	545	522
-7	764	786
-6	1057	1121
-5	249	161
-4	1623	1545
-3	766	759
-2	279	232
0	827	874
1	346	378
2	1390	1379
3	312	304
5	526	518
6	1227	1253
9	530	551
10	308	283
11	260	223
12	805	811
14	761	746
15	336	363

2,5,L

-15	329	360
-14	477	517
-13	675	680
-10	864	855
-7	674	594
-5	1211	1154
-4	1061	1044
-3	751	713
-2	1679	1626
-1	738	736
0	990	967
1	541	598
2	216	196
4	622	681
7	1019	1013
8	518	558
9	424	417
10	367	370
11	577	573
13	367	435
16	419	490
17	465	438

2,6,L

-16	613	645
-15	566	573
-14	339	369
-13	508	502
-12	981	1019
-10	451	487
-9	220	140
-6	225	303
-4	922	964
-3	1090	1105
-2	406	420
1	811	793
2	184	151
3	534	568
5	690	734
6	1557	1390
8	201	167
9	763	753
10	404	376
11	852	868
12	625	643
14	791	819
15	363	376
16	308	352

2,7,L

-14	760	725
-13	510	515
-12	372	341
-11	701	615

2,7,L

-10	547	556
-8	356	364
-7	408	338
-5	865	887
-4	627	623
-3	378	349
-2	471	428
-1	1051	983
0	487	467
1	204	251
4	1407	1374
5	839	852
6	438	421
7	982	952
8	680	676
9	404	395
13	749	732
15	361	364

2,8,L

-15	423	364
-14	301	317
-13	484	412
-12	640	615
-7	280	301
-5	627	655
-4	429	413
-3	1447	1436
-2	458	453
-1	1031	1048
0	591	541
2	1270	1224
3	1325	1362
4	501	477
5	1493	1490
6	935	959
7	339	313
12	247	276
15	375	406

2,9,L

-14	475	467
-13	435	402
-11	688	681
-9	523	555
-5	824	822
-3	417	379
-1	243	252
1	1031	1019
4	696	697
5	548	517
7	1115	1096
8	396	367
10	321	289
11	512	506
13	546	520
14	334	415

2,10,L

-13	273	245
-10	269	243
-9	958	933
-7	940	956
-6	380	367
-4	520	443
-2	742	737
-1	1131	1127
3	927	904
5	240	217
6	422	369
9	621	615
11	314	333
12	317	328

2,11,L

-11	662	671
-8	274	219
-7	1266	1155
-5	518	475
1	1297	1267
2	423	347
3	292	267
5	230	313
6	290	300
11	333	307

2,12,L

-9	1044	1045
-5	335	336
-2	243	268
-1	275	277
3	675	609
4	242	215
5	314	321
9	361	343

2,13,L

-7	864	778
-6	344	336
-5	357	315
-1	419	458
1	820	779
2	342	311
4	518	495
5	279	273
7	351	420

2,14,L

-1	439	415
0	354	371
3	726	659

3,0,L

-16	839	835
-14	573	592
-12	588	618
-8	1245	1233
-6	827	815
-4	582	660
-2	444	429
0	2554	2457
2	864	803
4	1040	1063
6	717	726
8	444	435
10	1369	1369

3,1,L

-18	678	696
-16	370	369
-10	768	759
-9	332	288
-8	336	324
-7	518	472
-6	1438	1458
-5	457	471
-4	1036	1020
-2	417	406
-1	1267	1233
0	1710	1674
1	323	384
2	1536	1519
3	795	777
4	1023	965
5	342	342
6	1016	1017
7	407	367
8	1183	1243
10	674	656
11	343	453
12	820	817
14	369	363

3,2,L

-16	477	460
-14	267	274
-12	428	457
-10	499	448
-9	479	439
-8	1204	1193
-7	355	365
-6	1002	976
-3	231	196
-2	234	338
-1	711	668
0	1292	1317
1	469	422
2	580	588
3	1437	1419
4	1122	1170
5	1144	1137
8	835	832
9	298	317
10	1596	1634
12	472	487
13	245	217
14	321	291
16	280	290

3,3,L

-16	310	341
-14	410	437
-12	510	516
-11	365	372
-10	1002	997
-9	667	672
-7	1063	1053
-6	1101	1111
-5	1397	1309
-4	2423	2396
-1	496	511
0	425	496
1	634	601
2	1093	1087
3	1188	1137
4	216	219
5	350	389
6	1127	1032
7	241	198
8	860	879
9	1145	1182
11	567	575
12	914	955
14	569	548

3,4,L

-16	341	356
-14	479	449
-10	662	676
-8	1008	1020
-6	487	471
-5	1585	1557
-4	1265	1256

Table 3.6a continued

3,4,L

-2	1220	1219
-1	1350	1311
0	1030	1029
1	566	576
2	883	879
3	557	595
4	499	535
5	1145	1125
6	600	591
7	867	836
8	270	211
9	269	337
10	499	451
11	449	461
14	306	326
16	431	450
17	354	405

3,5,L

-15	463	463
-13	657	659
-12	886	857
-10	467	496
-9	647	652
-8	1557	1493
-7	1404	1333
-6	1588	1546
-5	232	259
-4	1426	1416
-3	841	889
-2	723	676
-1	198	131
0	1252	1227
1	1501	1452
2	886	822
3	192	172
5	1002	1032
6	750	757
8	336	337
9	1003	975
11	332	334
12	326	307
13	565	535
14	453	416
15	325	339

3,6,L

-15	355	344
-14	391	363
-13	474	523
-11	777	789
-10	661	734
-9	316	339
-8	275	253
-7	451	413
-5	710	716
-2	1142	1173
-1	824	820
0	541	589
1	348	394
2	196	226
3	527	487
4	519	503
5	781	766
7	1141	1136
8	549	553
9	236	297
10	490	509
11	257	299
13	411	382
15	490	513
16	612	592

3,7,L

-12	711	721
-10	287	288
-9	639	605
-7	335	295
-5	464	423
-4	694	714
-3	1526	1567
-2	207	177
-1	949	909
0	607	596
3	1483	1423
5	1336	1314
6	805	823
7	551	529
8	452	484
9	294	282
11	440	459
12	316	396
14	429	433

3,8,L

-14	622	593
-13	566	575
-12	393	287
-11	631	619
-9	667	639
-5	528	525
-3	303	283
-2	696	677
-1	286	309
1	438	471
3	262	301
4	256	269
5	693	735
6	301	341
7	1121	1165
8	326	309
9	512	558
12	304	279
13	703	784

3,9,L

-14	351	415
-13	273	306
-9	390	401
-8	733	639
-7	378	384
-6	432	405
-5	349	336
-3	551	511
-1	837	938
0	671	697
2	497	482
3	932	927
5	998	1009
6	490	496
9	374	369
11	358	346
12	382	419

3,10,L

-11	686	656
-9	311	325
-8	327	342
-7	600	590
-5	430	428
-4	319	289
-3	776	719
-1	365	369
1	876	951
2	404	421
5	338	350
7	236	278
8	617	594
11	336	434

3,11,L

-11	290	328
-9	835	820
-7	524	529
-5	230	204
-4	371	396
-3	530	548
-1	1166	1218
1	333	306
3	769	786
4	326	335
5	355	348
11	331	279

3,12,L

-7	381	375
-5	625	636
-2	301	281
-1	355	345
1	1051	1086
2	252	275
3	580	556
4	246	246
5	508	465

3,13,L

-7	522	504
-3	396	405
-2	373	367
-1	618	596
0	339	342
2	316	371
3	693	676
4	287	262
6	299	264

3,14,L

-1	231	253
1	833	803

4,0,L

-16	500	519
-10	1394	1063
-8	741	736
-6	1860	1896
-4	1059	1020
-2	1193	1180
0	732	668
2	4129	4071
4	349	345
6	1590	1516
8	1428	1430
10	672	649
12	712	709

4,1,L

-16	573	545
-14	616	614
-12	433	443
-10	357	299
-9	442	451
-8	1711	1726
-6	918	911
-4	1130	1112
-3	525	551
-2	862	859
0	912	921
1	816	783
2	375	355
3	418	453
4	846	916
5	1035	1013
6	967	988
7	462	336
10	722	755
11	226	228
12	372	395
13	309	289
16	305	311

4,2,L

-17	397	404
-16	546	578
-12	442	402
-11	248	230
-10	1101	1083
-9	895	837
-7	507	546
-6	1483	1467
-5	615	592
-4	506	526
-3	321	291
-2	289	306
-1	671	617
0	1109	1122
1	790	795
2	447	516
4	554	478
6	952	949
7	266	251
8	1525	1553
9	785	782
10	444	472
11	434	393
12	867	810
14	393	371
17	322	283

4,3,L

-14	553	577
-10	282	295
-9	270	246
-8	1466	1449
-7	873	865
-6	628	632
-5	585	626
1	718	752
2	477	469
3	665	698
4	842	936
6	575	639
7	1291	1292
8	226	232
9	430	429
13	271	253
15	249	292
16	523	502

4,4,L

-13	333	316
-12	702	693
-10	961	917
-9	454	485
-7	844	844
-6	1245	1262
-4	986	1000
-3	899	903
-2	313	285
-1	628	659
0	592	610
1	429	399
2	690	707
4	706	753
5	991	1003
6	814	777
7	456	448
9	803	854
11	226	227
12	363	415
13	281	265
14	537	522
17	362	337

4,5,L

-15	369	396
-11	574	549
-10	817	809
-9	903	915
-8	915	874
-7	445	403
-6	307	318
-5	527	555
-4	810	844
-2	1527	1552
-1	1170	1157
0	1395	1879
1	752	752
2	469	469
3	698	698
4	936	936
6	639	639
7	1292	1292
8	232	232
9	429	429
13	253	253
15	292	292
16	502	502

4,6,L

-13	780	766
-12	732	746
-11	325	339
-10	312	311
-9	846	856
-7	644	647
-5	548	495
-4	1099	1127
-3	521	553
-2	648	642
-1	526	499
1	476	420
3	254	303
4	1131	1087
5	933	1000
6	362	446
8	355	337
9	813	870
11	546	526
12	372	401
14	598	613

4,7,L

-14	422	380
-11	1312	1341
-10	245	231
-9	599	574
-6	279	281
-5	495	492
-3	521	533
-2	902	928
-1	859	811
0	452	488
1	643	653
2	491	508
3	513	511
4	344	379
5	265	278
6	335	355
7	1226	1246
9	529	502
13	292	282
15	505	499

4,8,L

-13	427	443
-8	305	245
-6	401	373
-4	522	534
-3	1015	1047
-1	543	536
0	532	556
1	227	221
3	440	481
5	1035	1039
6	514	559
7	367	353
8	413	414
10	292	292
14	385	388

4,9,L

-13	589	564
-12	266	291
-11	673	715
-10	221	220
-5	323	371
-4	603	639
-3	475	521
1	522	572
2	675	659
3	293	287
5	380	372
7	814	831
8	303	355
9	437	493
10	558	543
12	422	469
13	586	596

4,10,L

-11	282	195
-9	594	608
-7	319	246
-3	481	488
-2	278	225
-1	1025	1063
0	562	561
1	334	359
3	599	578
5	362	362
8	268	256
9	382	377
11	437	494

4,11,L

-11	318	312
-8	271	249
-7	665	695
-6	261	242
-5	1017	946
-3	600	631
0	226	127
1	1103	1078
3	666	612
7	229	159

4,12,L

-9	455	516
-7	781	747
-4	322	318
-3	650	671
-1	852	893
3	562	585
5	337	352

4,13,L

-5	633	634
-3	546	544
-1	257	234
1	907	858
2	250	236
3	474	453

4,14,L

-1	362	406
0	404	419

5,0,L

-16	460	501
-14	1415	1434
-12	832	853
-8	1389	1393
-6	1195	1212
-4	212	251
-2	1213	1127
0	785	753
2	2429	2343
4	2135	2154
6	1486	1493
8	203	243
10	1231	1242
12	1140	1097
14	409	353
16	568	549

5,1,L

-16	564	566
-13	612	592
-12	530	516
-10	886	824
-9	270	318
-7	224	332
-7	395	391
-6	1513	1555
-4	835	836
-1	1105	1063
1	292	294
2	1527	1437
3	496	461
4	361	397
5	671	660
6	869	848
7	204	206
8	964	980
10	399	398
12	558	576
14	359	390

5,2,L

-14	576	587
-13	415	454
-12	291	372
-2	1355	1382
-7	1100	1059
-6	749	757
-5	664	650
-4	746	692
-2	948	960
-1	803	785
0	521	553
1	413	391
3	1376	1340
4	1270	1320
5	1000	976
6	1201	1191
7	811	823
8	371	363
10	960	989
12	695	728
16	341	319

5,3,L

-16	514	541
-13	392	375
-12	443	444
-10	927	855
-9	1211	1207
-8	304	311
-7	392	425
-6	517	569
-4	1327	1315
-3	802	806
-2	315	340
-1	875	880
0	454	471
1	468	434
2	1382	1431
3	1051	982
5	668	716
6	806	870
8	703	743
9	694	712
10	225	307
13	273	308
14	376	348
17	419	393

5,4,L

-15	297	297
-14	596	624
-11	652	651
-10	257	257
-8	969	992
-7	599	560
-6	760	752
-4	729	774
-3	354	378
-2	1603	1631
-1	739	728
0	1829	1788
1	1100	1097
3	1120	1121
4	1235	1241
5	383	389
6	485	526
7	1040	1068
8	339	318
13	323	351
16	437	407

5,5,L

-12	247	212
-11	612	603
-10	484	406
-9	501	515
-8	536	489
-6	661	684
-5	193	85
-4	698	782
-2	260	277
-1	724	705
2	930	932
3	471	510
5	1038	1106
8	924	903
9	808	822
16	403	426

5,6,L

-11	1000	1020
-10	463	442
-9	865	830
-8	522	505
-6	415	392
-5	659	619
-4	325	404
-3	747	769
-2	755	857
0	1034	1078
3	429	456
5	347	395
6	733	746
7	1090	1051
9	340	355
10	423	429
11	384	415
15	507	522

5,7,L

-13	633	653
-12	769	766
-11	479	520
-8	264	218
-6	546	508
-4	404	378
-3	824	788
-2	248	230
-1	732	744
0	485	484
1	360	376
4	183	235
5	867	934
6	407	401
7	342	346
8	649	640
9	330	351
10	576	590
11	620	647
14	457	434

5,8,L

-14	388	407
-13	602	563
-11	983	968
-10	547	547
-9	722	668
-6	415	456
-5	354	384
-3	426	416
-1	1028	1023
0	350	329
1	256	211
3	302	341
5	462	433

5,12,L

-5	661	674
-3	716	705
1	978	987
3	879	868

5,13,L

-5	440	381
-3	432	410
-1	471	437
3	469	493
4	240	255
5	335	250

6,0,L

-16	629	669
-12	668	684
-10	684	631
-8	252	278
-6	1090	1113
2	2550	2552
4	969	987
6	667	732
8	744	789
10	207	288
14	532	523
16	454	490

6,1,L

-16	353	295
-14	1245	1243
-12	635	600
-9	225	198
-8	1448	1448
-7	785	760
-6	791	812
-2	175	187
0	1103	1069
1	902	917
2	217	182
3	890	864
4	1853	1910
5	951	934
6	585	590
8	428	439
10	708	751
12	885	809
14	244	219
16	473	452

6,2,L

-16	637	696
-14	345	385
-12	513	521
-10	899	899
-9	369	398
-6	767	838
-5	453	441
-4	1114	1080
-3	305	299
-2	494	551
0	429	424
1	215	294
2	1815	1886
5	578	643
6	743	782
10	393	379
11	309	296
14	645	683

6,3,L

-15	329	600
-14	294	295
-12	588	569
-11	335	372
-9	299	321
-8	822	846
-7	975	898
-6	811	774
-5	1185	1140
-3	577	629
-2	843	863
-1	307	282
0	912	915
1	650	834
2	428	497
3	1154	1131
4	875	931
5	654	429
6	904	957
11	354	399
12	470	448
15	260	254
16	361	408

6,4,L

-13	751	801
-10	532	559
-9	577	594
-8	371	420
-7	304	306
-6	625	603
-4	1085	1133
-3	405	392
-2	767	716
-1	664	707
0	440	448
2	923	972
3	413	433
4	892	913
5	559	622
7	360	367
8	995	979
9	661	619
10	500	454
14	251	320

6,5,L

-11	775	773
-9	269	286
-8	232	207
-4	440	457
-3	560	614
-2	1043	1114
0	738	851
1	203	350
3	441	467
4	406	419
6	1246	1254
7	813	851
8	544	571
11	294	385

6,6,L

-13	571	579
-12	705	654
-11	376	343
-10	481	534
-9	518	566
-8	492	488
-7	476	567
-5	227	349
-4	1273	1245
-1	766	736
0	529	502
1	461	460
2	341	411
3	829	822
7	314	336
8	957	997
9	560	536
10	473	498
11	303	270
13	364	334

Table 3.6a continued

6,6,L

14	361	347

6,7,L

-11	602	686
-9	572	603
-8	343	345
-5	321	322
-3	594	602
-2	1094	1097
2	429	426
5	424	408
6	657	656
7	853	877
8	497	456
9	496	541
10	504	541
13	341	343

6,8,L

-13	582	571
-12	380	392
-10	779	743
-9	436	566
-8	374	333
-7	525	582
-6	365	362
-5	496	496
-4	419	407
-3	608	623
-1	1133	1138
0	463	474
1	535	547
3	439	479
5	705	745
7	503	555
8	643	664
11	628	608
12	445	414

6,9,L

-11	551	533
-9	550	511
-8	273	282
-6	501	515
-5	410	403
-4	623	633
-3	570	591
1	724	730
2	334	306
3	357	405
4	206	203
7	578	590
9	712	733
10	513	497
12	481	510

6,10,L

-7	694	742
-5	274	269
-3	719	692
-1	906	938
0	352	393
1	562	555
2	210	73
5	651	693
7	382	344
8	260	272
11	669	619

6,11,L

-6	309	318
-5	979	1031
-4	253	207
-3	555	536
1	598	600
3	913	915
5	224	239
7	219	107
9	385	347

6,12,L

-7	689	689
-3	559	547
-1	461	449
3	489	494
5	442	437

6,13,L

-3	257	298
1	707	715
3	623	610

7,0,L

-16	302	319
-14	1255	1191
-12	1267	1249
-8	1697	1669
-6	1466	1439
-4	723	736
-2	1296	1259
0	273	308
4	741	816
8	723	767
10	618	658
12	1053	1036
14	492	471
16	384	403

7,1,L

-16	607	595
-14	345	313
-12	506	459
-10	727	724
-9	476	437
-6	788	800
-4	1274	1284
0	216	173
1	506	481
2	1815	1815
3	182	170
4	1213	1258
6	302	316
7	501	509
8	233	251
10	422	407
14	813	823
15	471	443
16	391	301

7,2,L

-15	358	311
-14	767	737
-13	308	292
-12	331	352
-9	447	455
-8	610	650
-7	768	769
-6	941	939
-5	308	347
-4	515	553
-3	675	681
-2	916	997
0	682	733
1	692	737
2	844	849
4	912	907
5	353	380
6	667	668
7	444	427
8	545	520
11	206	59
12	1022	1068
13	396	374
15	261	214
16	560	593

7,3,L

-15	262	70
-13	447	436
-12	394	395
-10	660	705
-9	423	405
-8	394	425
-7	399	335
-4	447	436
-3	203	261
-2	401	425
-1	1115	1113
0	993	961
1	539	514
2	1460	1497
3	272	222
4	936	933
6	911	910
7	290	292
8	659	632
10	439	447
13	594	636
14	657	676
15	316	311

7,4,L

-15	242	384
-12	403	411
-11	541	536
-8	514	526
-7	353	398
-5	395	358
-3	754	776
-2	1252	1277
-1	463	463
0	780	836
1	1134	1161
2	341	301
3	617	633
4	1427	1399
6	954	975
8	404	375
9	404	420

7,5,L

-13	479	439
-12	349	355
-11	328	329
-10	496	537
-9	612	652
-8	638	606
-7	240	266
-6	245	224
-5	407	401
-4	981	951
-3	408	428
7	289	268

7,8,L

-12	729	724
-11	787	784
-9	1066	1069
-5	410	434
-7	281	308
-6	467	377
-5	351	328
-4	488	501
-3	415	427
-1	279	312
0	196	41
1	422	427
2	208	236
3	275	290
6	404	426
7	561	550
8	312	314
9	910	925
10	433	429
13	304	265

7,9,L

-11	333	279
-7	881	925
-4	557	615
-3	800	825
-2	245	241
-1	676	636
0	288	249
1	445	484
3	324	326
5	526	603
6	274	226
7	553	548
11	679	649
12	291	280

7,10,L

-9	429	431
-5	1068	1075
-4	484	505
-3	572	539
0	462	444
1	400	387
2	256	228
3	781	822
7	335	344
9	572	576
10	357	393
7	618	620
8	447	458
10	218	223
12	245	200
14	696	646

9,2,L

-14	667	636
-13	325	303
-12	556	563
-7	305	279
-6	639	667
-4	368	367
-3	451	439
-2	1000	976
0	1126	1192
1	910	939
2	651	672
3	304	284
4	207	204
6	644	658
7	541	592
8	379	369
9	403	403
11	242	227
12	651	574
13	234	109
14	364	390

9,3,L

-15	296	322
-14	434	490
-12	479	439
-11	717	693
-10	469	419
-8	566	589
-4	403	424
-3	454	460
-2	743	744
2	686	735
3	251	848
4	775	769
8	785	770
10	738	719
11	588	601
13	455	421
14	418	366

9,4,L

-12	522	559
-10	274	258
-6	353	351
13	526	522

9,7,L

-10	729	748
-8	488	537
-7	653	685
-6	348	355
-1	786	802
1	674	709
5	441	417
7	554	510

9,8,L

-11	531	571
-9	785	789
-8	731	744
-6	243	182
-3	347	320
0	446	403
3	276	249
7	504	517
9	705	687
10	320	385

9,9,L

-10	267	288
-9	243	212
-7	561	566
-6	460	503
-5	414	426
-3	222	267
-2	539	560
-1	554	539
1	608	583
3	262	252
5	479	454
6	416	425
7	467	442

9,10,L

-8	255	316
-5	502	503
-3	427	429
-2	396	344
0	312	323
3	773	753
4	252	222
5	316	321
7	561	525

9,11,L

-5	280	299
-4	232	183
-3	378	371
1	402	441
2	263	363
5	734	833

9,12,L

-2	224	115

10,0,L

-14	376	350
-12	600	644
-4	1844	1906
-2	1356	1427
2	386	400
4	873	857
6	314	304
8	225	197
10	229	209
14	529	490

10,1,L

-14	531	520
-12	727	747
-6	1236	1283
-5	243	225
-4	784	781
-2	757	742
0	593	646
2	408	383
3	402	382
4	263	279
6	639	671
8	406	385
9	212	76
10	387	406
12	745	714
14	313	231

10,2,L

-14	508	536
-13	237	212
-11	335	353
-9	319	309
-8	612	592
-4	1349	1346
-2	711	745
0	317	309
1	338	401
2	423	421
3	553	570
4	907	919
6	459	458
8	535	482
10	577	578
13	459	443
14	499	498

10,3,L

-14	357	377
-12	583	562
-11	445	462
-10	324	346
-8	263	213
-6	700	722
-4	355	370
-3	223	350
-2	507	535
0	388	383
1	943	990
2	572	557
3	463	494
4	314	327
6	552	535
8	534	514
9	361	353
11	435	349
12	555	581
13	323	371
14	471	433

10,4,L

-13	268	301
-11	424	468
-10	510	467
-9	338	323
-8	692	705
-7	426	390
-6	304	272
-4	306	291
2	570	615
3	1004	951
4	510	530
5	550	539
7	228	213
8	429	421
9	254	238
10	914	916
11	661	659
13	393	455

10,5,L

-12	474	439
-10	535	465
-9	475	482
-7	244	196

Table 3.6a continued

10,9,L

-5	252	301
-3	556	547
-1	486	556
0	335	392
1	461	454
2	396	413
3	650	630
4	419	408
5	245	282
6	285	300
7	298	357
8	541	559
9	374	334
11	296	314
12	430	521

10,8,L

-10	433	423
-8	682	524
-7	744	746
-5	709	674
-2	611	626
-1	931	946
0	343	353
1	923	896
2	926	933
3	349	356
4	591	637
7	650	598
8	361	372
9	589	620
10	401	425

10,7,L

-9	793	727
-8	564	534
-7	424	423
-6	422	401
-3	467	513
-2	390	399
-1	339	405
0	918	885
2	690	764
4	418	465
5	241	248
9	339	379
9	455	486

10,8,L

-9	365	359
-7	783	757
-6	457	474
-5	416	398
-1	757	797
0	545	544
1	756	779
2	477	521
3	264	310
5	421	474
6	435	426
7	312	556
10	221	134

10,9,L

-9	567	586
-8	382	375
2	453	454
3	364	368
5	241	199
7	358	421

10,10,L

-7	255	263
-6	575	597
-4	351	351
-3	254	271
-2	351	273
-1	542	511
0	533	531
1	429	409
5	526	511
7	765	738

10,11,L

-3	484	414
2	247	195
3	453	421

11,0,L

-12	562	606
-6	1051	1092
-4	1001	992
-2	1059	1085
2	228	296
6	847	885
8	692	690
10	456	480
12	661	624

11,1,L

-9	450	413
-8	352	312
-5	243	272
-4	1153	1141
-2	1277	1287
1	392	418
3	454	423
4	775	727
6	679	708
8	215	297
10	260	284

11,2,L

-12	627	601
-9	279	406
-8	290	311
-6	655	676
-5	370	408
-4	633	582
-3	218	193
-2	716	680
0	1049	1089
1	494	546
2	562	517
3	245	266
6	511	521
8	523	541
12	505	504

11,3,L

-11	552	570
-10	375	398
-7	420	492
-6	603	618
-5	456	397
-4	374	346
-4	635	671
-2	556	594
2	321	268
3	277	302
4	577	596
6	266	218
7	235	159
8	538	569
10	499	500
11	522	467
13	251	255

11,4,L

-12	480	479
-10	252	364
-9	469	473
-7	465	462
-6	572	577
-5	368	368
-4	267	297
-2	238	238
0	491	472
2	536	514
3	535	512
5	320	307
6	767	871
8	435	424
9	616	602
12	373	347

11,5,L

-10	485	448
-8	720	684
-7	580	544
-6	638	615
-5	424	427
1	749	726
3	467	457
6	566	594
7	525	532
8	714	684
9	279	282
10	597	545

11,6,L

-9	412	431
-8	366	346
-6	361	289
-5	468	458
-3	564	554
-2	278	336
-1	649	688
0	656	595
2	1084	1143
3	561	592
4	247	246
5	673	690
8	242	252
9	294	279

11,7,L

-8	430	473
-7	453	463
-5	419	390
-2	273	292
-1	518	538
0	353	354
1	606	620
3	368	367
4	622	633
6	378	371
8	343	306
10	306	302

11,8,L

-9	652	626
-7	526	544
-6	406	411
-3	550	621
-2	254	297
1	227	203
2	467	514
3	646	632
4	358	387
5	355	325
9	315	344

11,9,L

-7	529	475
-6	494	483
-5	614	595
-2	493	549
-1	783	772
0	479	531
1	788	772
2	279	431
5	524	493
7	423	363

11,10,L

-3	522	535
-1	518	521
1	380	401
3	479	636
4	231	205
5	295	289

12,0,L

-12	384	361
-10	592	603
-8	222	219
-4	1055	1065
-2	1026	1061
4	806	769
6	787	826
8	478	579
10	412	448

12,1,L

-12	737	679
-10	369	385
-8	301	280
-7	286	256
-6	493	525
-4	565	580
-3	353	340
-2	426	411
0	577	581
1	270	316
2	447	421
4	227	256
6	705	718
8	644	633
10	386	383
12	332	334

12,2,L

-11	374	353
-10	286	304
-8	521	499
-5	231	305
-4	467	461
-2	1277	1264
-1	223	30
4	704	700
5	386	390
6	871	828
7	290	314
8	493	463
10	301	328
11	353	340

12,3,L

-10	444	409
-8	300	289
-7	471	441
-6	627	660
-4	690	680
0	686	661
2	315	298
3	453	485
4	362	366
6	668	608
8	554	540
9	364	367

12,4,L

-10	351	365
-9	664	654
-8	725	713
-7	468	460
-5	662	631
-2	469	480
-1	406	429
3	383	393
8	695	717
10	663	674

12,5,L

-10	351	310
-9	470	555
-7	349	340
-6	417	466
-5	845	873
-4	634	642
-3	452	470
0	490	539
5	404	372
8	311	305

12,6,L

-7	506	501
-3	429	431
-1	619	646
1	657	698
2	675	713
3	330	402
4	349	372
8	337	321
9	611	630

12,7,L

-9	457	438
-8	326	322
-7	476	453
-6	577	610
-4	392	373
-3	483	469
-1	471	506
0	563	539
2	635	712
3	581	547

12,8,L

-7	320	338
-5	439	464
-2	409	376
-1	365	340
1	834	875
2	280	233
3	438	441
5	443	395
7	454	465

12,9,L

-3	538	538
-1	605	559
0	434	439
3	799	798
4	273	236
5	385	399
-1	307	264
3	302	277
5	511	513
7	279	290
8	291	234

14,5,L

-7	395	376
-6	577	538
-5	325	334
-4	439	424
-3	273	311
-1	402	410
2	502	475
3	521	530

14,6,L

-6	697	686
1	630	653
3	444	374
4	359	364
5	248	295

14,7,L

-4	388	385
2	506	470
3	463	502

15,0,L

-6	443	388
-2	416	463
0	559	564
2	528	485
6	573	556

15,1,L

-2	398	326
0	427	439
2	276	324
4	675	673
6	514	536

15,2,L

-6	405	381
-4	568	561
-3	213	126
0	576	558
2	639	621
6	316	307
-6	479	448
-5	321	315
-2	645	602
0	381	297
4	487	504
5	275	297
6	351	276

15,4,L

-6	297	313
-4	662	665
-2	324	340
-1	336	389
1	401	424
2	471	465
3	419	460
5	345	345

15,5,L

1	387	377
3	615	551

16,0,L

-2	562	525
0	607	601
4	373	322

16,1,L

-2	282	230
-1	339	392
0	581	576
2	389	376

16,2,L

-2	585	541
-1	254	241
0	698	664
3	224	209

16,3,L

-2	467	462
-1	306	227
0	311	327
1	250	286
2	550	535
10	663	674

12,5,L

-10	351	310
-9	470	555
-7	349	340
-6	417	466
-5	845	873
-4	634	642
-3	452	470
0	490	539
5	404	372
8	311	305

12,6,L

-7	506	501
-3	429	431
-1	619	646
1	657	698
2	675	713
3	330	402
4	349	372
8	337	321
9	611	630

12,7,L

-9	457	438
-8	326	322
-7	476	453
-6	577	610
-4	392	373
-3	483	469
-1	471	506
0	563	539
2	635	712
3	581	547

12,8,L

-7	320	338
-5	439	464
-2	409	376
-1	365	340
1	834	875
2	280	233
3	438	441
5	443	395
7	454	465

12,9,L

-3	538	538
-1	605	559
0	434	439
3	799	798
4	273	236
5	385	399

13,0,L

-10	652	656
-6	596	562
-4	725	749
-2	213	250
0	477	516
2	265	279
6	767	744
8	1028	1053

13,1,L

-10	248	266
-8	449	587
-6	259	213
-5	307	280
-4	716	701
-3	378	348
-2	1112	1147
-1	315	364
0	454	488
1	387	373
4	843	842
6	803	802
10	566	506

13,2,L

-10	670	659
-8	381	372
-6	687	674
-4	369	377
-2	297	295
-1	508	456
0	323	283
1	646	675
2	403	407
4	410	388
6	520	535
8	556	512
10	220	192

13,3,L

-10	454	474
-9	609	600
-8	573	553
-2	470	496
-1	500	455
0	247	205
3	197	110
4	469	437
5	536	522
6	391	398
7	367	450
8	513	452
10	455	443

13,4,L

-10	331	307
-9	405	375
-7	389	422
-5	247	239
-4	470	463
-2	343	321
0	240	203
1	556	549
4	314	321
6	343	357
8	531	523

13,5,L

-8	741	743
-7	336	369
-6	608	613
-5	406	446
-2	417	438
0	406	429
1	502	507
3	400	399
4	236	234
5	493	453
7	365	326
9	356	352

13,6,L

-7	332	302
-6	477	453
-5	463	425
0	591	594
2	444	412
3	612	627
4	245	194
5	443	442

13,7,L

-7	542	533
-5	568	564
-2	543	521
-1	379	357
1	774	727
2	321	358
3	576	603

13,8,L

-3	333	289
0	412	434
3	435	450

14,0,L

-10	278	248
-8	305	298
-2	484	445
0	469	530
4	858	816
6	482	443

14,1,L

-9	378	402
-6	257	258
-4	723	674
-2	363	330
-1	553	556
0	322	338
1	420	388
2	696	754
6	738	746
8	763	764

14,2,L

-9	257	259
-8	385	381
-5	207	102
-2	623	600
-1	639	629
4	896	891
5	297	319
6	609	594

14,3,L

-7	348	359
-6	685	679
-4	469	462
0	476	472
1	559	597
2	256	240
3	361	341
5	508	529
6	370	360
8	414	443

14,4,L

-6	494	509
-5	478	411

Table 3.6b: Structure factors for cis,trans-Ru(PhCOS)$_2$(PMe$_2$Ph)$_2$(phen)

Columns are 1, $10|F_o|$, $10|F_c|$

0,0,L

4	517	592
6	-98	121
10	1228	1246
12	1993	1921
14	1338	1398
16	668	767
18	329	351
20	-149	58
22	475	459

0,1,L

1	-58	101
2	1618	1457
3	814	804
4	703	717
6	364	427
7	171	150
8	455	514
10	892	926
11	363	316
12	189	221
13	504	514
14	651	667
15	331	312
16	810	771
17	380	375
20	748	687
22	379	377

0,2,L

0	3667	3510
1	245	208
2	600	766
3	381	404
4	510	381
5	413	409
6	193	204
7	159	132
9	-89	135
10	604	572
12	1213	1225
13	291	286
14	573	590
15	206	200
16	240	158
17	241	189
21	190	163
22	294	284

0,3,L

1	1502	1357
3	1446	1269
4	1010	945
5	-54	38
6	212	195
8	835	820
10	823	887
14	724	656
16	467	428
19	-119	77
20	453	426
21	246	206

0,4,L

0	3166	3015
1	352	307
2	1745	1685
3	466	426
4	154	160
5	792	759
6	724	637
7	275	266
10	565	549
11	413	347
12	1442	1441
14	1006	978
16	756	692
17	330	351
19	466	439
20	234	244

0,5,L

1	-113	51
2	556	504
3	-101	129
4	877	867
5	341	310
6	766	772
7	234	248
8	1574	1417
9	262	291
10	902	871
11	254	203
12	-160	62
13	320	344
14	466	430
15	287	265
16	336	355
17	312	303
18	450	423
19	251	258
20	570	561

0,6,L

0	622	662
1	571	511
2	467	470
3	-149	178
4	163	115
6	297	364
7	332	329
8	426	439
9	306	286
10	540	580
11	351	342
12	520	540
14	415	413
16	361	354
17	301	252

0,7,L

4	194	180
6	291	313
8	393	426
10	233	199
11	209	190
12	-67	6
14	221	158
17	-162	161

0,8,L

0	489	525
1	214	154
2	467	531
4	321	271
5	186	192
8	630	630
9	195	228
10	570	575
11	-144	111
12	448	412
14	466	437

0,9,L

2	289	292
3	452	462
4	605	617
5	233	265
6	870	811
7	239	144
8	598	580
9	307	387
10	-160	166
11	-122	157
12	-98	163

0,10,L

4	355	362
6	627	595
8	546	516
10	1322	1344
12	795	812
14	-25	137
16	496	446
18	437	388
20	444	444

0,11,L

3	252	197

1,0,L

2	213	153
-2	886	875
4	2439	2439
-4	1781	1713
-6	849	852
8	1138	1398
-8	1435	1401
10	1337	1337
-10	1322	1327
12	448	415
-12	283	224
-14	1525	1391
16	535	530
-16	829	778
18	718	734
-18	323	216
20	651	735
-20	358	233
22	391	331
-22	717	617

1,1,L

0	3582	3551
-1	179	233
2	1983	2345
-2	1552	1603
3	513	539
-3	157	143
4	414	415
-4	866	797
5	346	367
-5	311	297
6	561	598
7	421	365
-7	198	139

1,1,L

9	514	534
10	495	547
-10	1003	1061
11	652	649
-11	422	434
12	1480	1447
-12	1676	1613
14	865	861
-14	816	836
15	237	241
-15	476	433
16	729	692
-16	294	272
17	421	429
18	412	426
-18	324	263
-19	213	174
20	234	155
-22	531	538

1,2,L

0	591	629
1	751	740
-1	310	340
-2	775	689
3	996	971
-3	240	187
4	1300	1265
-4	645	524
5	257	276
-5	712	688
-6	556	526
7	783	736
-7	628	622
8	699	752
-8	298	373
9	259	329
-9	317	276
10	811	776
11	542	541
-12	-122	172
-13	177	223
14	-150	125
-14	1212	1187
15	255	228
-15	217	187
16	222	266
-16	928	897
-17	274	263
18	557	588
20	749	741
-20	285	330
-22	565	566

1,3,L

0	1358	1295
1	168	132
-1	275	275
-2	1255	1213
-3	211	171
4	640	657
-4	1047	1022
5	349	367
-5	332	256
6	1043	1062
-6	767	620
7	564	517
8	1275	1292
-8	1176	1202
9	621	554
-9	430	445
10	1380	1333
-10	609	582
11	793	283
-11	-162	122
14	386	345
-14	916	854
16	229	285
-16	614	528
17	232	293
18	368	396
20	701	629
-20	435	362
-21	-82	80

1,4,L

0	1350	1362
1	208	239
2	711	651
-2	1644	1631
-3	163	157
4	1054	1073
-4	822	846
5	188	204
6	534	475
-6	258	210
7	540	507
-7	354	329
8	683	634
-8	557	551
10	973	966
-10	1162	1181
11	311	237
12	1074	1063
-12	1230	1148
14	830	836
-14	911	902
-15	270	195
16	525	534
-16	316	325
-20	220	193

1,5,L

0	527	554
1	233	245
-1	516	578
2	253	267
-2	445	338
-3	256	214
-6	152	134
7	194	156
-7	238	217
10	336	353
-10	271	275
-11	198	243
12	233	257
-13	184	154
14	191	153
-14	372	339
-16	321	255
17	385	379

1,6,L

0	898	882
1	-123	28
-1	616	632
2	248	153
-2	860	818
4	484	513
-4	980	881
-5	394	418
6	842	789
-6	726	714
8	769	773
-8	654	623
9	276	267
10	763	759
-10	238	263
11	279	255
-11	398	377
13	357	355
-13	451	445
-14	336	317
15	332	287
-16	401	357

1,7,L

0	527	554
1	233	245
-1	516	578
2	253	267
-2	445	338
-3	256	214
-6	152	134
7	194	156
-7	238	217
10	336	353
-10	271	275
-11	198	243
12	233	257
-13	184	154
14	191	153
-14	372	339
-16	321	255
17	385	379

1,8,L

-1	-130	59
-4	336	297
6	406	400
-6	598	521
-7	255	215
8	481	463
-8	415	375
9	426	358
-9	451	444
10	434	419
-11	302	250
14	-161	117

1,9,L

0	536	535
1	323	351
-1	265	252
2	619	599
-2	777	753

1,9,L

4	579	581
-4	436	430
6	230	216
7	-95	48
-7	-53	36
8	213	265
-8	620	575
10	456	490
-10	635	604
-11	-151	195
12	533	502
-12	309	331

2,0,L

0	2328	2272
2	3725	3933
-2	3009	3035
4	2624	2750
-4	1250	1151
6	354	351
-6	273	206
8	1116	1119
-8	1181	1143
10	635	662
-10	2222	2152
12	1117	1146
-12	2377	2759
14	1163	1173
-14	618	657
16	1130	1067
-16	368	351
18	610	761
-18	414	356
-20	236	136
22	324	339
-22	492	440

2,1,L

0	1048	1022
1	141	51
-1	561	531
2	1367	1316
-2	1359	1224
3	425	420
-3	247	230
4	1354	1404
-4	1852	1832
5	148	166
-5	660	667
6	1243	1295
-6	541	602
7	288	256
8	2059	2174
-8	767	721
9	288	255
10	1322	1344
-10	718	703
11	226	221
-11	295	258
12	282	267
-12	955	922
13	335	348
-14	1414	1488
-15	476	455
-16	1133	1066
-17	320	245
18	581	516
20	820	781
-20	121	114
21	-152	164
-22	555	532

2,2,L

0	535	531
1	565	555
2	664	613
-2	1520	1479
-3	1681	1691
4	1014	1117
-4	386	384
5	557	615
7	547	568
-7	560	466
8	332	340
10	311	443
-10	611	670
11	234	251
-11	277	231
12	161	153
-12	1255	1171
14	186	220
-14	183	200
16	340	373
-17	196	139
18	320	290
-18	401	346
-19	231	172
20	-168	213
-21	250	244
-22	492	451

2,3,L

0	848	856
1	1257	1188
-1	2536	2490
2	219	168
-2	1140	1134
-3	315	324
4	258	351
-4	1211	1160
5	438	409
-5	404	373
6	426	431
-6	524	575
7	232	343
-7	161	159
8	583	675
-8	351	387
10	300	335
-10	612	580
11	487	462
-11	652	611
-12	369	376
-13	546	519
-14	815	765
15	-130	64
-16	693	641
17	511	492
18	573	554
20	569	540
-20	305	284

2,4,L

0	2405	2333
1	530	520
-1	1512	1443
2	1200	1231
-2	1386	1357
-3	333	315
4	1433	1425
-4	232	218
5	333	326
-5	419	400
6	491	524
-6	835	757
7	475	438
8	155	117
-8	818	874
9	-139	124
10	539	535
-10	979	941
11	307	327
12	881	833
-12	1234	1159
13	234	229
-13	416	435
14	683	735
-14	661	627
-15	232	238
16	793	793
-17	483	431
18	623	556
-18	-49	47
19	432	422
20	-99	156
-20	319	286

2,5,L

0	1241	1231
-1	162	228
2	233	294
-2	1239	1231
-3	757	721
4	803	738
-4	859	843
5	188	170
-5	261	230
6	1182	1223
-6	1038	986
7	528	531
8	1521	1495
-8	521	541
9	767	756
-9	228	180
10	1343	1378
-10	233	210
12	377	398
-12	191	182
-14	525	551
-15	388	380
-16	843	838
17	-75	25
18	423	421
-18	530	518
19	217	251

2,5,L

-20	403	398

2,6,L

0	872	825
1	566	595
-1	728	803
-2	1256	1236
3	317	264
4	509	522
-4	555	538
-5	551	541
-6	307	284
7	411	418
-7	679	669
8	169	169
-9	393	378
10	424	415
-10	373	332
11	407	428
12	392	415
-12	509	544
-14	385	397
16	313	260
18	255	298
-19	295	272

2,7,L

0	368	440
-1	298	322
-2	474	415
-3	-143	170
-4	695	677
5	304	301
6	203	186
-6	517	496
-8	373	357
-8	272	274
9	345	357
10	472	481
13	265	240
-13	-82	111
-16	359	343

2,8,L

0	264	214
1	215	253
-1	498	536
-2	579	617
4	517	514
-4	-117	167
-6	378	387
7	257	288
-9	-102	67
10	451	401
-10	412	432
11	-120	126
12	513	561
-12	368	357
-13	265	259
14	452	452

2,9,L

0	305	357
-1	340	358
-2	521	540
-3	305	158
4	354	303
-4	837	842
-5	267	253
6	602	617
-6	755	756
7	251	280
-7	-100	154
8	782	768
-8	386	378
9	272	264
10	747	776
12	333	322

2,10,L

0	260	243
1	308	324
-1	284	253
2	427	394
-2	346	384
4	318	256
5	202	205
-6	-52	27
-10	220	285

2,11,L

4	-85	24

3,0,L

0	525	505
2	831	843
-2	652	708
4	902	903
-4	3124	3162
6	2016	2132
-6	1445	1363
8	2576	2551
-8	1996	1909
10	726	857
-10	697	679
12	623	671
-12	907	818
14	704	704
-14	982	942
-16	804	700
18	645	652
-18	123	69
20	818	785
-20	276	265
-22	181	146

3,1,L

0	1415	1415
1	387	370
2	225	208
-2	291	307
3	277	293
-3	173	193
4	2584	2672
-4	1060	994
5	303	306
-5	576	505
6	1383	1452
-6	685	715
-8	1012	992
-9	212	219
-10	1292	1315
11	-76	113
12	260	306
-12	1393	1379
13	351	334
-13	-117	24
14	496	528
-14	351	344
-15	321	298
16	966	1000
18	642	662
-18	-162	120
-19	196	194
-20	432	355
-22	445	464

3,2,L

0	515	499
1	314	301
-1	376	305
2	151	93
-2	219	216
3	245	266
-3	2133	2034
4	263	255
-4	1493	1532
5	383	433
6	993	1000
7	231	152
-7	551	497
8	1921	1916
-8	519	578
9	284	299
-9	928	824
-10	-138	141
-11	175	175
12	130	132
-12	657	575
-13	163	225
14	306	261
-14	930	938
-15	415	435
-16	1350	1337
18	481	481
-18	354	359
-19	192	182
20	548	568

3,3,L

0	792	779
1	257	259
-1	685	635
2	787	831
-2	554	529
3	675	628
4	544	595
-5	730	657
6	253	224
-6	846	854
7	565	548
-7	595	673
-8	851	873
9	599	674
-9	153	134
10	-124	232
-10	622	559
-11	198	235
-12	930	909
13	175	122
-13	513	499
14	253	231
15	281	292
-15	574	533
16	741	751
17	195	153
18	491	531

Table 3.6b continued

3,3,L

-20	369	283

3,4,L

0	1341	1446
1	654	655
-1	324	349
2	431	434
-2	1655	1657
3	436	424
-3	420	385
4	816	779
-4	2132	2120
6	1144	1212
-5	903	920
7	240	240
8	1852	1861
-8	635	585
9	515	583
-9	317	237
10	940	581
11	262	247
-11	592	603
12	422	398
-12	499	485
-13	331	308
14	362	380
-14	622	631
-15	269	270
-16	733	762
17	274	237
18	562	610
-18	590	563
-19	214	219
20	636	643
-20	334	351

3,5,L

0	1251	1226
1	378	393
-1	610	632
2	1145	1147
-2	1127	1144
3	478	493
-3	433	472
4	1454	1469
-4	469	498
5	269	231
-5	843	786
6	974	978
-6	1227	1225
-7	515	526
8	188	151
-8	556	560
10	402	408
-10	419	413
11	354	355
12	522	508
-12	774	756
13	266	256
14	432	447
-14	204	157
16	778	779
18	477	469
-20	134	146

3,6,L

0	419	338
-2	1065	1128
3	437	432
-3	329	250
-4	967	940
5	564	548
-6	565	565
-7	758	814
9	807	808
-8	213	191
9	214	257
-9	322	294
10	605	612
-10	-67	33
12	273	302
-12	264	285
-14	423	418
-15	530	522
-16	665	667
18	265	251
-18	536	558

3,7,L

0	157	180
1	342	311
-1	888	876
-2	-166	230
3	220	220
5	360	355
6	81	59
-6	488	421
7	360	329
10	-155	150
-10	214	154
11	293	344
12	351	368
-13	351	383
14	309	309
16	129	163

3,8,L

0	424	372
-2	673	708
-4	442	458
5	-111	113
-6	405	417
8	514	557
-8	-134	160
9	351	361
-9	429	438
10	498	474
-10	-110	70
-11	302	287
-12	296	294
-13	-121	106
-14	376	394
-15	225	210

3,9,L

0	619	530
-1	662	651
2	498	440
-2	462	501
3	-53	69
4	609	612
-4	181	144
6	485	497
-6	318	296
8	257	252
-8	362	307
10	-148	148
-10	417	378
11	-127	244
12	423	403
-12	462	463
-13	284	318

3,10,L

0	441	414
-2	745	747
-4	618	622
-5	-162	142
6	235	266
-6	428	418
7	228	194
8	465	473
-10	-75	74

3,11,L

-3	-105	72

4,0,L

0	481	495
2	1563	1717
-2	742	695
4	907	982
-4	332	312
6	2523	2565
-6	2275	2231
8	541	531
-8	3153	3234
10	381	343
-10	993	1025
12	495	516
-12	594	568
14	714	650
-14	693	659
16	1495	1466
18	1136	1117
-18	277	293
20	381	432
-20	546	514
-22	526	556

4,1,L

0	795	824
1	-116	82
-1	336	236
2	513	435
-2	1185	1216
-3	-123	138
-4	1520	1537
6	1483	1434
-6	1252	1122
7	394	398
-7	869	877
8	2618	2738
-8	492	511
9	290	335
-9	593	569
10	433	473
-10	439	432
11	411	449
-11	521	478
-12	358	376
14	485	479
-14	879	899
16	208	171
-16	838	755
17	-78	121
18	439	438

4,2,L

0	301	349
-1	525	527
2	558	574
3	923	889
-3	906	817
4	801	866
-4	-37	70
5	663	699
-5	1172	1096
6	1133	1265
-6	943	958
7	-74	54
-7	852	803
-8	857	820
9	529	562
-9	245	175
10	349	379
-11	-58	20
-12	534	543
-13	-99	105
-14	287	296
15	-09	44
16	485	478
18	435	478
19	-68	71
-19	248	196
-20	515	491

4,3,L

0	255	250
1	1040	996
-1	209	169
2	224	243
-2	297	308
3	435	480
-3	1140	1132
4	225	275
-4	756	793
5	381	425
-5	791	760
6	713	711
-6	563	558
-7	773	721
8	1061	1106
-8	373	385
-9	856	765
10	317	323
-11	706	662
-12	461	469
-13	173	207
14	432	476
-14	724	723
16	-103	26
-16	681	661
-18	388	394
-18	521	524
20	468	514

4,4,L

0	908	878
1	743	654
-1	956	858
2	1165	1155
-2	446	420
-3	730	732
4	1021	1113
-4	523	519
5	165	155
-5	362	380
6	1201	1251
-6	1525	1471
-7	155	150
8	866	850
-8	1317	1229
9	-154	206
10	-148	88
-10	764	773
-11	455	426
12	454	472
-12	521	523
-13	829	816
14	671	650
-14	234	256
-15	342	359
16	745	750
-16	166	181
18	573	560
-20	315	295

4,5,L

0	854	877
-1	594	560
2	422	372
-2	1322	1318
-3	921	934
-4	1526	1559
6	636	675
-6	1133	1068
7	264	241
-7	712	761
8	1011	1110
-8	315	388
9	533	543
10	982	1033
-10	-134	158
11	319	347
12	602	619
-12	454	440
-13	314	244
14	564	578
-14	734	725
-15	677	651
-16	875	829
18	290	297
-18	512	507
-19	415	402

4,6,L

0	865	851
1	-113	6
-1	292	281
2	727	736
-2	844	755
3	-00	129
-3	569	548
4	325	330
5	330	351
-5	980	945
6	545	559
-6	426	462
7	506	488
-7	616	565
8	407	436
-8	367	370
9	249	265
10	-72	122
-10	412	400
11	202	204
12	219	224
-12	586	536
14	482	463
-14	351	396
16	364	340
17	-25	86
-17	436	461
-18	-133	186

4,7,L

0	314	312
1	257	212
-1	247	222
-2	855	825
4	-156	129
-4	435	444
-5	176	157
6	211	238
-6	373	352
7	236	254
-7	191	196
8	243	253
9	277	234
-9	271	215
10	279	253
11	-156	35
-11	475	481
-12	322	333
-14	552	532
-15	344	337
16	-136	98
-16	565	553
-17	-133	133

4,8,L

0	402	415
1	-132	78
-1	539	576
2	488	472
-2	195	145
3	216	231
4	421	374
-4	623	619
5	333	329
6	538	497
-6	493	497
7	-117	123
8	345	375
-8	391	432
-10	298	238
-11	197	213
12	184	136
-12	404	374
-13	328	393
14	394	342

4,9,L

0	512	543
-1	-58	56
-2	976	1050
-3	433	475
-4	521	523
6	333	278
-6	394	443

4,9,L

8	540	537
9	273	227
10	647	673
12	515	493

4,10,L

-1	-172	276
-2	-155	64
4	332	390
-4	-70	73
5	245	255
6	299	265
-7	237	226
-8	164	238

4,11,L

0	263	253
1	-152	117
-2	380	403

5,0,L

0	1345	1321
2	1689	1743
-2	1659	1668
4	-162	179
-6	1301	1353
6	1625	1573
-6	776	805
8	1431	1528
-8	313	223
10	1336	1415
12	570	515
-12	592	587
14	1035	1031
-14	580	576
16	514	504
-16	722	727
18	223	227
-18	440	473
20	411	580
-20	225	199

5,1,L

0	748	726
1	-134	72
-1	596	575
2	690	879
-2	531	455
3	483	457
-3	746	745
4	1837	1854
-4	802	755
5	578	652
6	1082	1095
-6	2138	2074
7	-115	52
8	713	733
-8	1957	1932
10	221	248
-10	408	465
12	-121	39
-13	325	285
-14	462	457
15	264	243
-15	380	377
16	564	533
17	-157	154
-17	420	415
18	728	763
-18	566	565
-19	269	246
20	386	389
-20	636	555

5,2,L

0	545	567
1	-75	141
-1	521	524
2	483	451
-2	1237	1214
-3	236	203
4	536	464
-4	1356	1389
5	363	362
6	655	620
-6	868	862
7	-50	33
-7	820	823
8	467	523
-8	473	462
-9	233	261
10	324	311
11	-58	35
-12	414	353
13	-102	62
-14	621	659
15	-127	137
-15	233	150
-16	947	913
17	263	250
18	337	287
-18	331	371
19	-130	134
-19	347	299
20	447	408
-20	-133	58

5,3,L

0	334	376
-1	876	897
3	-54	53
4	775	797
-4	236	255
5	-138	180
6	978	1007
-6	1162	1102
-7	523	535
8	646	670
-8	1713	1698
9	220	253
-9	224	253
-10	544	516
-11	309	354
12	276	268
13	-76	37
-13	486	486
14	522	560
-14	291	333
15	289	304
-15	185	202
16	505	557
-16	351	326
18	514	534
-18	498	505
20	186	194
-20	543	535
-21	213	183

5,4,L

0	768	788
1	329	342
-1	147	121
2	352	434
-2	816	856
4	487	486
-4	951	897
5	314	337
6	862	824
-6	1009	1014
7	330	312
8	1148	1193
9	427	411
-9	748	743
10	712	735
-11	670	665
12	928	937
-12	665	644
13	377	432
-13	-90	150
14	521	569
-14	834	851
-16	814	783
17	-152	184
18	337	328
-18	228	227
-19	276	235

5,5,L

0	556	535
-1	-73	39
2	952	988
3	323	315
-3	453	448
4	1441	1461
-4	653	714
-5	458	484
6	1591	1596
-6	733	714
-7	273	255
8	1338	1386
-8	1328	1113
-9	214	235
-10	605	592
-12	611	655
-13	245	239
14	654	638
-14	247	232
15	244	256
-15	-98	222
16	568	595
-16	430	425
-17	373	382
18	533	544
-18	347	347

5,6,L

0	339	438
2	-152	81
-2	607	379
3	327	332
-3	438	453
4	-122	135
-4	641	678
5	286	259
-5	181	177
-7	765	752
8	343	378
-8	-75	94

5,6,L

9	-147	144
10	323	345
12	627	648
-13	351	390
14	234	239
-14	620	589
-15	421	425
-16	555	551
17	265	281
-18	242	241

5,7,L

-1	-81	123
3	177	197
4	150	126
-4	343	390
-5	354	328
-6	311	318
8	216	216
-8	434	466
-9	187	205
-10	194	180
-13	297	291
-16	314	357

5,8,L

0	749	809
1	182	292
-2	823	615
-3	572	540
4	-143	148
-4	363	411
5	232	208
-5	469	454
6	305	317
7	319	359
-9	-23	119
10	341	294
12	402	405
-12	269	260
-14	514	511
-15	295	289

5,9,L

0	277	260
-1	-110	206
2	596	636
3	257	242
4	644	603
-4	381	410
5	315	314
-5	364	318
-6	451	427
-7	290	299
7	201	238
-7	318	252
8	402	394
-8	267	280
-10	327	314
11	-43	57
-12	285	275

5,10,L

0	600	614
1	-141	118
-2	658	636
-3	206	189
-4	335	352
6	228	259

6,0,L

0	904	827
2	708	655
-2	727	650
4	2542	2567
-4	881	878
6	1824	1544
-6	2217	2225
8	1295	1270
-8	1675	1720
10	508	520
-10	336	360
12	-54	30
-12	-118	116
14	531	547
16	883	927
-16	152	172
18	1015	1080
-18	668	665
20	640	648
-20	660	615

6,1,L

0	949	925
1	620	650
2	1051	1134
-2	1365	1352
3	419	447
-3	547	521
4	945	982
-4	1834	1836
5	-55	26
-5	1063	1096
6	574	604
-7	353	331
8	626	693
-8	385	439
-9	526	554
10	880	913
12	788	843
-12	355	350
13	222	272
14	702	713
-14	404	394
16	320	357
-16	879	879
17	-172	199
18	200	144
-18	348	332
19	-181	187
-19	210	237
20	353	333

6,2,L

1	371	334
-1	440	404
-2	309	361
3	266	320
-3	1042	963
4	1101	1166
-4	659	689
6	859	923
-6	1148	1147
7	331	312
-7	407	352
8	225	272
-8	1264	1293
10	-92	159
-10	596	586
-11	-101	169
-12	369	406
-14	222	248
-15	309	333
16	172	207
-16	400	362
-17	458	418
18	450	436
-18	729	773
19	-52	105
20	363	319
-20	689	669

6,3,L

1	358	389
2	358	410
-2	289	334
3	342	311
4	222	227
-4	734	860
5	316	352
6	448	470
7	498	503
-7	979	944
8	750	762
-8	253	263
9	-56	95
-9	591	559
10	435	420
-10	514	507
-11	423	428
12	535	532
-12	507	531
-13	238	231
14	360	354
-14	848	859
-15	404	395
-16	532	571
17	-167	224
18	249	279
-18	181	203
-20	-137	111

6,4,L

1	379	338
2	499	520
-2	-58	117
3	875	899
4	1293	1355
-4	732	715
5	530	550
-5	432	422
6	1243	1255
-6	1137	1116
8	761	803
-8	1373	1313
9	-115	49
10	536	547
-10	439	513
11	234	226
-11	613	593
-12	213	239
-13	335	345
14	229	252
-15	-133	67
16	837	856
-16	390	419
17	288	231
-17	-119	140

Table 3.6b continued

6,4,L

18	525	532
-18	534	522
-20	375	391

6,5,L

0	1368	1105
1	336	263
2	792	794
-2	1449	1374
3	260	239
-3	289	262
4	249	263
-4	1351	1302
6	265	333
-6	332	348
-7	235	196
8	622	609
-9	271	269
10	595	564
-10	353	314
11	-152	156
-11	254	256
12	765	818
-12	361	390
13	434	456
-13	354	383
14	565	571
-14	756	756
15	217	240
-15	236	276
16	365	352
-16	570	574
17	267	223
-19	234	242

6,6,L

0	-74	46
1	109	112
-1	467	420
2	350	306
-2	249	238
-3	410	422
4	858	927
-4	421	389
-5	626	601
6	629	645
-6	469	512
-7	625	618
8	225	296
-8	609	627
-10	658	638
11	348	359
-12	439	458
13	-166	147
15	365	385
-15	243	270
16	478	466
-16	368	332
-17	751	327
-18	376	372

6,7,L

0	426	418
-1	-52	154
-2	268	267
4	258	223
-4	292	285
6	364	376
7	342	320
8	233	194
-10	343	319
11	153	250
-11	-57	45
12	267	258
-12	535	551
13	239	226
-14	612	658
-16	461	461

6,8,L

0	-66	82
1	223	274
-2	437	356
3	435	463
-3	258	313
4	601	626
-4	485	505
6	422	406
-6	545	556
-7	181	192
8	272	280
-8	425	427
10	150	170
-10	507	530
11	232	200
-12	229	258
-13	333	353

6,9,L

0	783	767
2	418	425
-2	555	573
4	-42	71
-4	351	370
-5	334	346
7	216	244
10	409	350

6,10,L

-1	-169	210
2	324	306
4	380	381
5	226	207
-5	289	296
6	297	282

7,0,L

0	364	365
2	1110	1106
-2	690	737
4	1085	1109
-4	992	972
6	433	367
-6	408	393
8	1233	1286
-8	653	659
10	765	792
-10	986	974
12	1309	1275
-12	530	514
14	837	836
-14	525	525
16	356	272
-16	567	568
18	193	183
-20	423	423

7,1,L

1	561	592
-1	1214	1161
2	435	495
3	368	385
-3	165	213
4	814	863
-4	1327	1329
5	504	467
-5	169	193
6	1521	1542
-6	1569	1627
8	805	865
-8	1417	1391
10	439	380
-11	428	406
12	259	215

7,2,L

1	522	493
-1	535	517
2	367	436
-2	1428	1471
3	821	799
-3	546	534
-4	1242	1223
6	176	93
-7	360	336
8	571	579
-8	647	640
10	333	316
-10	544	553
12	353	353
-12	365	378
-13	379	331
14	344	336
-14	737	723
-15	-78	113
-16	803	827
18	242	258
-18	432	393
19	-37	72
-20	356	346

7,3,L

1	703	614
2	539	539
3	726	752
-3	606	556
4	998	1358
-4	684	714
5	487	459
-5	159	198
6	838	871
-6	1213	1226
8	432	433
-8	798	736
9	287	304
-9	437	441
-10	315	329

7,5,L

0	510	502
-1	692	700
2	549	601
-2	461	413
4	1246	1250
-4	694	714
5	369	439
6	1036	1114
-6	1069	980
-7	393	411
8	669	701
-8	668	664
-9	361	351
10	459	509
-10	924	936
11	514	531
-11	316	312
-12	315	259
-14	-164	137
-15	-140	203
16	502	520
-16	269	210
-18	480	436

7,6,L

0	505	561
1	-164	212
-1	313	295
2	535	462
-2	645	629
3	436	444
-3	350	339
-4	360	400
5	-55	37
6	357	388
-6	-148	187
7	207	224
-8	450	502
10	484	489
-10	277	341
11	-148	153
12	282	330
-12	424	380
13	210	243
14	506	513
15	-75	124
16	-54	128
-16	314	294
-17	252	244

7,7,L

-1	-166	201
2	216	201
3	356	371
4	481	436
5	324	333
6	336	371
-7	452	524
-8	314	358
9	217	126
-9	181	248
-10	506	594
11	315	314
-11	188	150
-16	328	359

7,8,L

0	539	499
2	477	449
-2	430	405
-3	282	249
5	304	320
-5	522	548
7	423	402
-7	283	297
12	321	300
-12	429	465

7,9,L

2	263	264
-2	395	365
4	555	557
-4	352	337
5	347	322
-5	213	175
6	647	667
-6	435	402
7	-181	177
-7	499	530
8	462	453
-8	401	373
-9	323	285
-10	381	428

7,10,L

0	397	388
2	295	283
-2	330	331

8,0,L

2	937	963
-2	610	624
4	934	950
-4	709	765
6	1524	1621
-6	1481	1443
8	1605	1620
-8	915	963
10	1040	1032
12	415	400
14	261	247
16	726	715
-16	547	557
18	536	514
-18	833	829
-20	473	436

8,1,L

0	414	444
1	248	287
-1	182	167
2	716	720
-2	774	794
3	303	277
-3	547	529
4	1120	1351
-4	1234	1176
-5	368	453
6	477	503
-6	349	332
-7	534	572
8	22	112
-8	712	746
9	326	355
-9	354	355
10	538	508
-10	738	815
11	297	337
-11	254	232
12	689	737
-12	539	544
-13	222	254
14	799	841
-14	773	795
-15	351	359
16	298	313
-16	671	655
18	-53	20
-20	519	491

8,2,L

0	448	539
1	176	134
-1	387	447
2	386	389
-2	696	537
3	221	243
-3	356	374
-4	813	834
6	542	514
-6	1485	1464
-7	-56	79
8	519	553
-8	831	859
10	315	429
-10	375	334
-12	183	172

8,3,L

0	332	351
-1	516	453
2	493	555
4	569	560
-4	512	490
5	540	553
-5	640	686
6	228	178
7	490	500
-7	414	240
8	357	344
-8	868	918
-10	592	642
11	-147	116
-11	351	319
12	333	416
-12	519	518
14	364	269
-14	327	339
-16	430	386
-17	-126	135
-19	-73	176

8,4,L

0	350	329
2	671	692
-2	674	704
3	957	992
-3	296	325
4	953	985
-4	904	920
5	722	741
-5	-93	29
6	1018	1031
-6	1139	1155
7	-73	7
-7	504	446
8	814	906
-8	693	713
9	367	332
-9	570	578
10	420	406
11	-183	175
-11	177	137
12	574	556
14	-166	59
16	420	462
-16	318	362
-18	662	658
-19	-168	142

8,5,L

0	1088	1054
1	374	378
2	810	868
-2	730	773
3	632	662
-3	268	239
4	650	612
6	-56	35
8	280	281
-8	664	673
-9	448	408
10	466	438
-10	318	302
-11	364	423
12	610	581
-12	370	409
13	-131	156
14	767	665
-14	172	168
16	474	451
-16	226	256
-18	-160	166

8,6,L

0	251	266
1	546	522
-1	566	566
2	362	350
-2	466	373
-3	-161	112
4	617	644
-4	513	534
6	568	565
-6	674	664
-7	333	306
8	432	423
-8	768	765
-9	241	247
-10	262	304
11	266	280
-11	444	469
-13	373	342
-14	262	246
-16	403	411

8,7,L

0	311	321
2	356	401
3	342	358
-3	-148	158
4	294	265
-4	-158	182
-5	-26	67
-6	352	330
7	237	244
8	-164	148
-8	402	419
-9	-156	209
10	185	175
-10	508	532
-12	583	596
13	-117	95
-13	-129	58
-14	289	279

8,8,L

0	280	266
-1	-100	97
-2	329	323
3	256	216
-3	293	318
4	393	399
-4	422	416
5	348	421
6	437	432
-6	429	346
-7	387	416
8	387	415
-8	526	557
-9	503	494
-10	282	305
11	-115	176
-13	182	121

8,9,L

0	459	473
2	490	449
3	277	301
-3	-124	185
4	350	367
-4	-100	120
5	-116	36
-8	222	243
-10	335	372
-12	466	458
14	307	296
-14	309	328

8,10,L

1	221	219
-3	262	249

9,0,L

0	513	526
2	1221	1236
4	783	847
-4	407	355
-6	470	439
8	375	326
-8	344	349
10	358	353
-10	635	601
12	782	833
-12	215	235
14	398	837
-14	259	239
-18	414	453
-20	458	475

9,1,L

0	439	458
1	546	635
-1	625	545
2	823	817
-2	1215	1233
3	443	447
4	869	933
-4	871	877
-5	106	96
6	832	796
-6	1154	1174
7	411	446
8	713	687
-8	536	526
-9	332	331
10	1336	1355
11	247	241
-11	549	533
12	335	475
13	273	213
-13	446	457
16	423	432
-16	555	549
-18	739	732
-20	373	435

9,2,L

-1	245	287
2	736	800
-2	312	336
3	-58	5
4	289	322
-6	314	281
7	-141	89
-7	-105	44
8	-117	115
-8	668	728
-9	455	483
10	212	256
-10	852	853
-11	479	429
12	712	689
-12	621	666
-13	180	101
14	460	516
-14	761	772
16	70	58
-16	500	482

9,3,L

0	-148	170
1	346	376
-1	105	110
2	516	496
-2	845	834
3	395	399
4	557	548
-4	689	680
5	501	480
-5	668	716
-6	976	990
-7	725	717
8	400	409
-8	893	840
-9	638	593
10	468	458
11	-150	191
-12	244	275
-14	325	345
-15	343	316
16	373	357
-16	718	732
-17	-139	175
-18	836	844
-19	-181	212

9,4,L

0	707	731
2	955	952
-2	212	175
4	761	806
5	-135	102
-5	645	624
6	413	411
7	350	330
-7	264	253
-8	562	545
-10	618	620
-11	411	395
12	833	850
-12	266	321
-13	-160	154
14	662	638
-14	367	313
16	361	364
-16	-95	110

9,5,L

0	325	234
1	561	557
-1	536	525
-2	646	648
4	358	474
-4	754	730
5	156	135
6	704	666
-6	865	877
-7	224	223
8	643	600
-8	876	847
10	561	551
-11	332	290
12	573	570
-13	327	331

9,6,L

0	545	541
-1	530	544
2	645	670
-2	268	262
3	432	456
-3	425	422
4	380	370
-4	324	387
-5	-73	165
8	-135	76
-8	489	510
-9	271	271
-10	622	618
-11	353	337
12	546	562
-12	466	458
14	307	296
-14	309	328

9,7,L

-1	212	219
3	267	265
4	263	248
-4	325	331
-5	247	259
6	327	293
-6	453	458
-7	291	236
-8	587	583
-9	-176	216
-13	-147	147
-14	332	361

9,8,L

0	377	332
1	349	335
2	528	542
3	289	284
-3	185	218
4	398	385
-4	-110	105
-5	315	344
6	259	277
-7	247	269
-8	412	428
9	243	244
-10	491	477
-12	307	319

9,9,L

0	-134	162
1	-33	17
-2	274	285
-3	-141	88
4	336	342
-4	325	356
-5	-144	181
6	457	432
-6	281	255

10,0,L

0	929	949
2	396	433
-2	1659	1619
4	912	895
-4	846	901
6	611	615
-6	575	732
8	401	437
-8	749	732
10	1115	1132
-10	252	239
12	1334	1317
-12	246	252
-14	373	418
-16	357	337
-18	642	646

10,1,L

0	982	979
2	1424	1341
-2	398	434
-3	428	443
4	323	339
-4	593	644
-5	455	434
-6	333	244
7	313	333
-7	439	434
8	493	465
-8	551	568
-9	555	547
-10	646	593
12	358	755
-12	582	713
13	-71	104
-13	268	315
14	783	738
-14	399	414
-15	233	267
16	249	251
-17	-154	132
-18	276	241

10,2,L

0	462	415
-1	318	328
-2	1123	1075
3	259	257
4	723	726
-4	713	754
-5	236	231
-6	538	555
-8	549	524
9	352	355
10	545	553
11	191	176
-11	268	257

Table 3.6b continued

10,2,L

12	583	627
-12	-154	238
14	233	233
-14	557	546
-15	-112	196
-16	570	575
-18	000	728

10,3,L

2	372	358
2	985	1009
-2	228	233
-3	435	478
4	414	418
-5	412	400
7	-129	159
8	414	426
-9	650	622
9	509	521
-9	191	154
-10	882	910
11	215	226
-11	-68	83
12	696	601
-12	622	639
14	554	557
-14	357	362
15	-74	10
-16	-149	55
-18	321	342

10,4,L

0	407	392
1	185	128
-2	707	701
4	385	364
-4	563	617
-5	434	428
6	528	570
-6	710	628
-7	617	622
8	468	483
-8	477	533
-9	228	160
10	800	788
12	468	465
-12	345	338
-14	321	300
-15	276	284
-16	336	299

10,5,L

0	624	556
-1	188	184
2	1051	1055
-2	-150	156
4	700	655
6	556	559
7	268	268
8	553	543
-8	392	365
-9	312	339
10	256	257
-10	744	754
-11	238	212
12	726	752
-12	312	261
14	672	648
-14	226	229

10,6,L

1	306	270
-1	461	463
2	-137	74
4	326	281
-4	451	459
6	446	523
-6	534	530
8	262	218
-8	314	333
10	234	241
-11	326	330
13	205	167
-14	253	290

10,7,L

0	324	296
-1	-67	101
2	645	645
4	412	508
-4	238	223
-5	207	168
6	225	221
-6	168	214
-8	457	508
9	-121	115
-9	-77	122
-10	606	648

10,8,L

0	158	150
-2	334	311
-4	598	498
5	-195	87
-5	294	293
6	514	493
-6	384	383
7	-97	72
8	378	330
-8	-119	115

10,9,L

0	265	289
1	297	314
2	409	402
-2	237	192
4	397	386

11,0,L

0	1048	980
2	1242	1205
4	694	676
-4	709	714
-6	-80	40
8	342	324
10	214	175
-10	607	642
12	551	507
-12	484	489
14	742	687
16	565	524
-16	307	324

11,1,L

0	1034	1015
1	498	452
-2	1323	1284
3	488	481
-3	-118	146
4	642	638
-4	496	554
5	442	457
-7	188	231
-8	437	463
-9	423	381
10	732	797
-10	317	283
11	-54	50
12	1031	1003
-12	461	446
14	-157	167
-14	597	603

11,2,L

0	1160	1128
2	1231	1234
3	-145	135
-3	202	194
4	477	454
-4	527	554
6	291	323
-6	264	220
7	433	298
8	534	472
-8	534	634
9	362	313
-9	-174	135
10	351	359
-10	1283	1327
-11	-129	83
12	549	557
-12	955	950
14	594	553
-15	-104	144
-16	136	154
-18	222	252

11,3,L

0	758	779
-2	822	853
3	329	323
4	379	392
-4	516	615
-5	431	486
-6	550	457
7	462	385
-7	736	696
-8	452	453
9	350	359
-9	199	255
10	535	524
-10	226	255
11	323	296
12	523	475
-12	703	559
-14	714	720
-16	450	490
-17	219	235

11,4,L

0	448	448
2	344	333
-3	241	246
4	581	553
5	204	192

11,4,L

6	401	406
-6	-100	23
8	485	464
-8	293	336
9	410	466
-9	257	268
-10	741	671
11	270	309
-11	-153	71
12	438	396
-12	441	471
13	-159	168
14	508	518
-16	-55	73

11,5,L

0	404	371
1	239	162
-1	-184	268
-2	531	511
4	344	276
-4	628	624
5	285	249
6	384	370
-6	220	212
-7	-112	48
8	393	394
-9	376	370
10	578	532
-10	-173	204
-11	248	303
12	531	509
-12	354	364
-14	256	267

11,6,L

0	350	353
2	503	534
-2	218	209
3	-168	7
4	536	529
-5	222	196
6	329	353
-6	-154	127
7	-145	217
-8	589	659
10	229	168
-10	757	774
11	-66	51
-12	469	506
-14	246	211

11,7,L

1	-76	108
-2	304	264
-4	456	483
-6	316	309
-9	188	205
-11	250	225

11,8,L

0	246	265
1	353	335
2	265	276
-2	-137	102
-3	-167	132
4	456	426
-5	244	262
-6	271	271
-8	550	555

12,0,L

0	1100	1105
2	345	352
-2	802	858
6	-168	179
-6	540	624
8	205	181
-8	605	479
10	953	969
12	805	814
-12	669	682
14	533	505
-14	661	656

12,1,L

0	768	723
1	478	432
-1	558	544
2	1075	1085
3	351	344
-3	417	448
4	356	360
-4	343	378
-5	417	405
6	665	635
-7	213	244
-10	1171	1252
12	347	421
-12	605	617
13	-25	42
-13	211	176
14	483	455

-16 447 425

12,2,L

0	950	870
1	316	336
-2	976	923
-4	466	443
5	333	268
10	523	414
11	237	237
-11	-175	177
12	422	422
-12	759	712
14	-147	160
-14	874	914
-16	309	353

12,3,L

0	486	501
1	313	319
-1	439	398
2	723	726
-2	-149	195
-3	280	275
4	418	429
-4	417	422
6	475	465
-6	201	219
-7	441	434
-8	341	344
-9	347	355
10	-129	178
-10	1039	1046
11	399	431
12	-182	186
-12	641	683
14	234	253
-15	198	153

12,4,L

0	850	874
2	306	274
-2	877	859
-3	418	395
-4	471	431
-5	444	442
8	392	407
10	672	719
-10	296	275
11	-184	240
12	548	564
-12	388	384

-13 -45 38

-14 383 424

12,5,L

0	523	522
2	558	551
-2	-18	34
4	532	534
-4	-137	94
-5	242	323
6	555	514
7	335	344
8	237	323
-8	448	437
9	213	143
-10	537	529
-12	291	338

12,6,L

0	394	337
1	-34	135
2	-35	133
-2	555	526
-3	227	135
-4	432	364
5	308	283
6	-159	53
7	233	218
8	374	359
9	-179	125
10	392	350
-10	-61	75
-11	284	315
-12	199	155

12,7,L

0	353	354
2	346	351
-3	-119	6
4	513	512
-4	222	176
5	-132	154
6	315	346
-6	427	421
-7	189	97
-8	533	659
-10	536	516

12,8,L

-2	378	349
-3	265	271
-4	455	408
-5	-149	183
-6	210	208

13,0,L

2	445	404
4	400	431
6	759	779
-6	261	268
-8	145	234
-10	612	649
-12	573	570
-16	277	231

13,1,L

0	937	887
1	-147	117
2	443	425
-2	789	746
3	288	279
4	417	406
-4	363	367
-5	340	273
-6	609	596
7	335	313
-7	337	346
8	308	267
9	-199	260
10	699	623
-10	432	445
12	420	433
-12	761	759
-13	-102	2
-14	667	683
-16	93	162

13,2,L

0	458	405
-1	275	246
2	754	719
4	485	454
-4	421	422
6	597	609
-6	288	286
-8	601	577
-9	-117	179
-10	965	994
-11	-27	15

-12 466 500

-16 405 458

13,3,L

0	867	816
1	265	277
2	422	430
-2	525	575
3	254	160
-3	514	492
-4	337	387
-5	423	365
-6	418	431
-7	271	203
10	632	614
-10	543	527
11	-150	223
-12	571	612
-14	661	664

13,4,L

0	420	349
-1	333	338
2	526	502
4	525	461
-4	365	356
6	434	430
7	-163	155
-8	278	219
-10	467	452
11	381	403
-12	239	276

13,5,L

0	466	400
-1	203	184
-2	676	682
-4	209	253
-6	-128	77
7	-178	247
-7	243	244
-8	-118	118
-9	-66	133
10	644	567
-12	-190	173

13,6,L

0	306	279
2	362	375
-3	228	208
-4	267	287
-5	265	276
6	440	375
-6	483	491
-8	495	479
-9	240	210
-10	449	485

13,7,L

0	304	339
-1	221	192
-2	485	501
-4	424	387
5	213	208
-6	213	250
-7	-97	82

14,0,L

0	568	536
2	626	615
-2	572	607
4	701	685
-4	522	462
-6	295	307
8	467	403
-8	393	362
10	513	489
-10	672	704
12	353	316
-12	470	466
-14	348	353

14,1,L

0	338	303
1	363	319
-1	305	319
-3	317	288
4	747	687
-4	217	263
-5	230	231
6	582	594
-6	343	288
8	429	415
9	269	304
-9	-71	170
-10	429	431
11	-231	202
-12	229	296

14,2,L

0	638	539
2	449	383
-2	824	799
4	455	433
-4	616	587
-6	333	346
7	373	359
8	534	435
9	-128	123
-9	294	253
10	435	417
-10	588	592
-11	-23	51
-12	798	739
-14	667	675

14,3,L

1	643	634
-1	380	333
-2	-138	159
4	507	491
-4	589	578
6	543	544
-6	570	556
7	243	227
-7	220	220
8	380	337
-8	249	269
-10	333	326
-11	343	363
-13	-157	175

14,4,L

0	624	335
-1	282	292
2	342	312
-2	533	527
-3	351	359
4	339	351
-4	312	323
8	322	252
-8	235	224
9	265	220
-9	-142	79
-12	601	662

14,5,L

-4	315	315
-6	392	325
8	352	336

14,6,L

-2	512	578
-4	414	357
5	372	350
-6	230	116
-7	260	266

15,0,L

2	-181	39
4	390	365
-4	459	393
6	729	668
-6	358	381
8	572	499

15,1,L

2	500	471
-2	659	632
-3	-128	83
-4	439	416
-5	-198	235
7	-149	155
-7	367	200
8	448	394
-8	317	200
-10	532	534
-12	375	394

15,2,L

4	391	412
-4	630	571
5	218	199
-5	-106	50
6	667	616
-6	765	794
7	-93	55

8 486 467

-8 377 422

-11 202 233

15,3,L

0	467	468
-1	388	357
2	533	504
-2	666	654
4	488	470
-4	458	472
-7	255	174
8	309	274
-10	545	601
-12	600	561

15,4,L

1	370	356
-1	251	245
4	154	253
-4	353	335
6	473	484
-6	400	434

15,5,L

0	305	289
-2	462	414
-4	257	303
-7	240	268

15,6,L

-3	322	343

16,0,L

0 -157 157

2 360 394

-2 515 492

4 524 538

6 318 259

-8 530 561

16,1,L

0	-138	158
1	-189	217
2	-186	235
-4	531	503
6	673	622
-6	614	648
-8	272	283
-11	-133	54

16,2,L

0	337	277
2	419	357
-2	622	617
4	448	442
-4	345	376
-5	354	281
-8	500	486
-10	532	520

16,3,L

1	228	245
-2	353	355
4	212	213
-4	694	661
-5	-109	10
6	629	563
-6	663	664
-8	355	271
-9	-186	167

15,4,L

0	97	131
2	-176	235
-2	335	248
-3	-142	133
4	340	336
-7	-113	69

17,0,L

-4	392	334
-6	518	517
-8	-160	153

17,1,L

1	-134	25
2	184	53
4	531	538
-4	-187	235
-6	-189	231
-8	458	474

17,2,L

0	214	238
1	-124	129
-2	403	338
-4	603	562
-6	593	585
-7	-117	21

17,3,L

0	389	365

CHAPTER 4

REACTION OF $Ru(PhCOS)_2(PMe_2Ph)_2$ WITH BIDENTATE PHOSPHORUS-DONOR LEWIS BASES, AND THE X-RAY ANALYSIS OF THE STRUCTURE OF ONE OF THE PRODUCTS

4(i) Introduction

In view of the unexpected stereochemistries found in the $Ru(PhCOS)_2(PMe_2Ph)_2(L_2)$ compounds where L_2 is a bulky, bidentate nitrogen-donor base such as 2,2'-bipyridyl or 1,10-phenanthroline, it was considered of interest to react $Ru(PhCOS)_2(PMe_2Ph)_2$ with bulky, bidentate phosphorus-donor bases, and to examine the spectroscopic properties and the structures of the products.

4(ii) Results and Discussion

(a) When $Ru(PhCOS)_2(PMe_2Ph)_2$ was reacted in ethanol with a 1:1 molar ratio of bis-diphenylphosphinomethane, a yellow product was obtained from a reaction mixture which smelt strongly of free tertiary phosphine; after recrystallisation from ethanol the maximum yield obtained was 38%. The i.r. spectrum indicates the presence of both S-bonded unidentate and bidentate monothiobenzoate groups, and the analysis figures agree best with the formula $Ru(PhCOS)_2(PMe_2Ph)_3$(mediphos). The sharp melting point of the compound, and the reproducibility of its analytical composition after recrystallisation, both suggest that it is a pure compound and not, for example, a mixture of $Ru(PhCOS)_2(PMe_2Ph)_3$ and free mediphos.

However, the $^{31}P-\{^1H\}$-n.m.r. spectrum at room temperature (see Table 4.2) exhibits a strong singlet at -22.11 p.p.m., the chemical shift of free mediphos, three poorly-resolved doublets between 1 p.p.m. and 5 p.p.m., and a broad triplet at 24.41 p.p.m. On cooling to 240K, the spectrum is resolved into three AX_2 patterns, identified as those

characteristic of a fresh solution of mer-$Ru(PhCOS)_2(PMe_2Ph)_3$ (see Chapter 5, section (ii)a, and Table 5.3). A possible overall mechanism for this reaction is shown in Scheme 4.1; it is proposed that the mediphos initially reacts with the $Ru(PhCOS)_2(PMe_2Ph)_2$ to form a chelated complex of the type $Ru(PhCOS)_2(PMe_2Ph)$(mediphos) (cf. the product formed with etdiphos which is discussed in section 4(ii)b). This step involves the displacement of a PMe_2Ph group and two molecules of this free phosphine then presumably attack the mediphos chelate to displace mediphos and give the meridional isomers of $Ru(PhCOS)_2(PMe_2Ph)_3$. This scheme is related to that proposed[99] for the reaction of $Ru(R_2PS_2)_2(PMe_2Ph)_2$ with carbon monoxide:

$$Ru(R_2PS_2)_2(PMe_2Ph)_2 + CO \longrightarrow Ru(R_2PS_2)_2(PMe_2Ph)_2(CO)$$

(trans-phosphines)

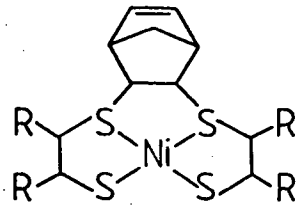
$$\downarrow$$

$$Ru(R_2PS_2)_2(PMe_2Ph)_2(CO) \longleftarrow Ru(R_2PS_2)_2(PMe_2Ph)(CO) + PMe_2Ph$$

(cis-phosphines)

where a molecule of PMe_2Ph leaves the complex then re-attacks to rupture a Ru-S bond and give the final product. In the present case, the product isolated always contains mediphos, although it is completely dissociated in solution to give mer-$Ru(PhCOS)_2(PMe_2Ph)_3$ and free mediphos. Two possible explanations can be suggested: either the product crystallises from ethanol as a clathrate containing a 1:1 molar ratio of the ruthenium complex and mediphos, or the mediphos is actually bound in the complex and dissociates immediately in solution. Complexes of the type $M(S\text{-}S)_2(C_7H_8)$ are known[117,118] (M = Ni, Pd or Pt; S-S = $Ph_2C_2S_2^{2-}$ or for Ni, $(CF_3)_2C_2S_2^{2-}$) where the diene is bonded to

two cis-sulphur atoms from neighbouring coordinated dithiene ligands (31).



R = Ph or CF_3

(31)

Analogous bonding of mediphos to cis-sulphur atoms in neighbouring monothiobenzoate ligands of $Ru(PhCOS)_2(PMe_2Ph)_3$ can be envisaged, but the immediate and complete dissociation of the mediphos in solution, and the presence of isomers of mer-$Ru(PhCOS)_2(PMe_2Ph)_3$ which are believed to contain trans-sulphur atoms (see Chapter 5, section (ii)a), suggests that a chlathrate structure in the solid state, or some other type of cocrystallisation, is more likely. An unambiguous answer must await an X-ray structure analysis.

(b) When $Ru(PhCOS)_2(PMe_2Ph)_2$ was reacted with a 1:1 molar ratio of bis-diphenylphosphinoethane in ethanol, a yellow-brown product was obtained which analysed for $Ru(PhCOS)_2(PMe_2Ph)$(etdiphos). The compound gave a non-conducting solution in CH_2Cl_2 and was shown by osmometric molecular weight measurements to be monomeric in chloroform and acetone solutions at several different concentrations. In the i.r. spectrum, $\nu_{(CO)}$ is observed at 1460 and 1545 cm^{-1}, suggesting that both S-bonded unidentate and bidentate monothiobenzoate groups are present; the $\nu_{(CS)}$ region is obscured by etdiphos vibrational modes.

The methyl region of the ^{1}Hn.m.r. spectrum (see Table 4.1 and Figure 4.1) shows four doublets at 1.25δ, 1.46δ (two doublets superimposed, on the evidence of decoupling experiments) and 1.78δ, each with

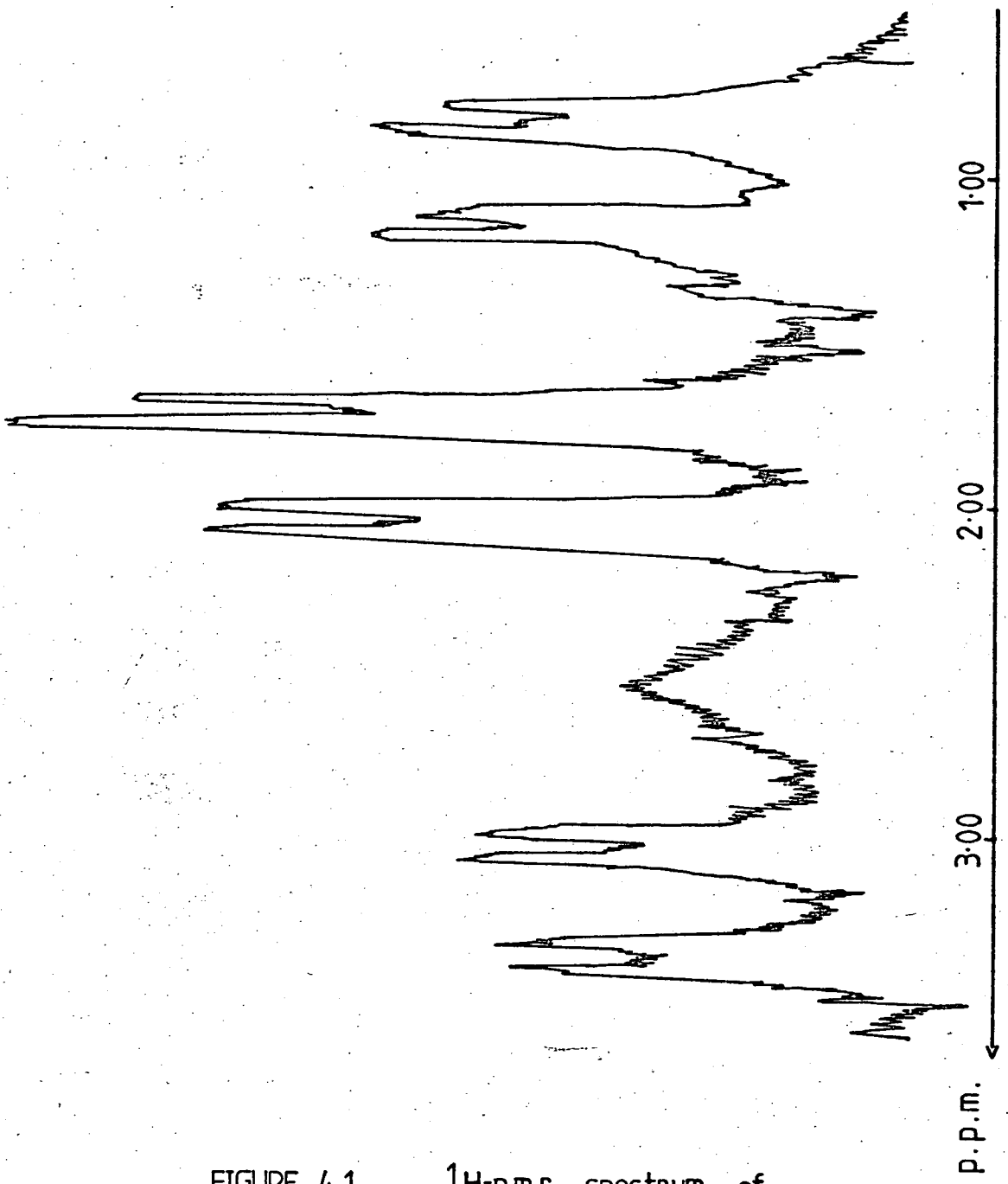
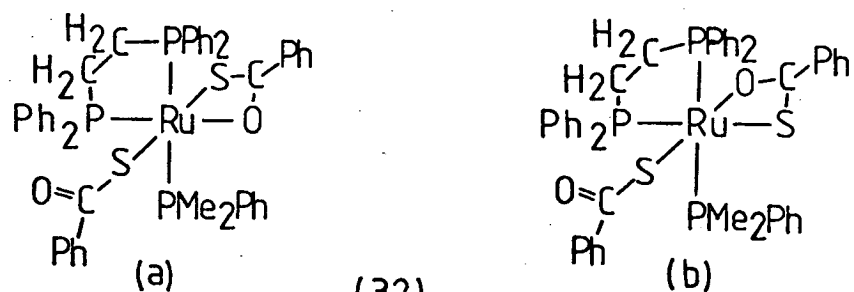


FIGURE 4.1 ^{1}H-n.m.r. spectrum of $Ru(PhCOS)_2(PMe_2Ph)_2$(etdiphos)

a J(PH) of 8.50 Hz and a smaller doublet splitting of 1.60 Hz on each peak. The doublet at 1.25δ and one at 1.46δ decouple when irradiated at a frequency equivalent to a ^{31}P chemical shift of ca 3 p.p.m., and the second doublet at 1.46δ and the one at 1.78δ decouple at ca 5 p.p.m. The smaller splitting of 1.6 Hz disappears on irradiation at ca 67 p.p.m. and irradiation at ca 1 p.p.m. and at ca 9 p.p.m. also has a visible effect on the pattern observed. The $^{31}P-\{^{1}H\}$-n.m.r. spectrum consists of two first-order ABX patterns of approximately equal intensity coupled thus (see Figure 4.2):

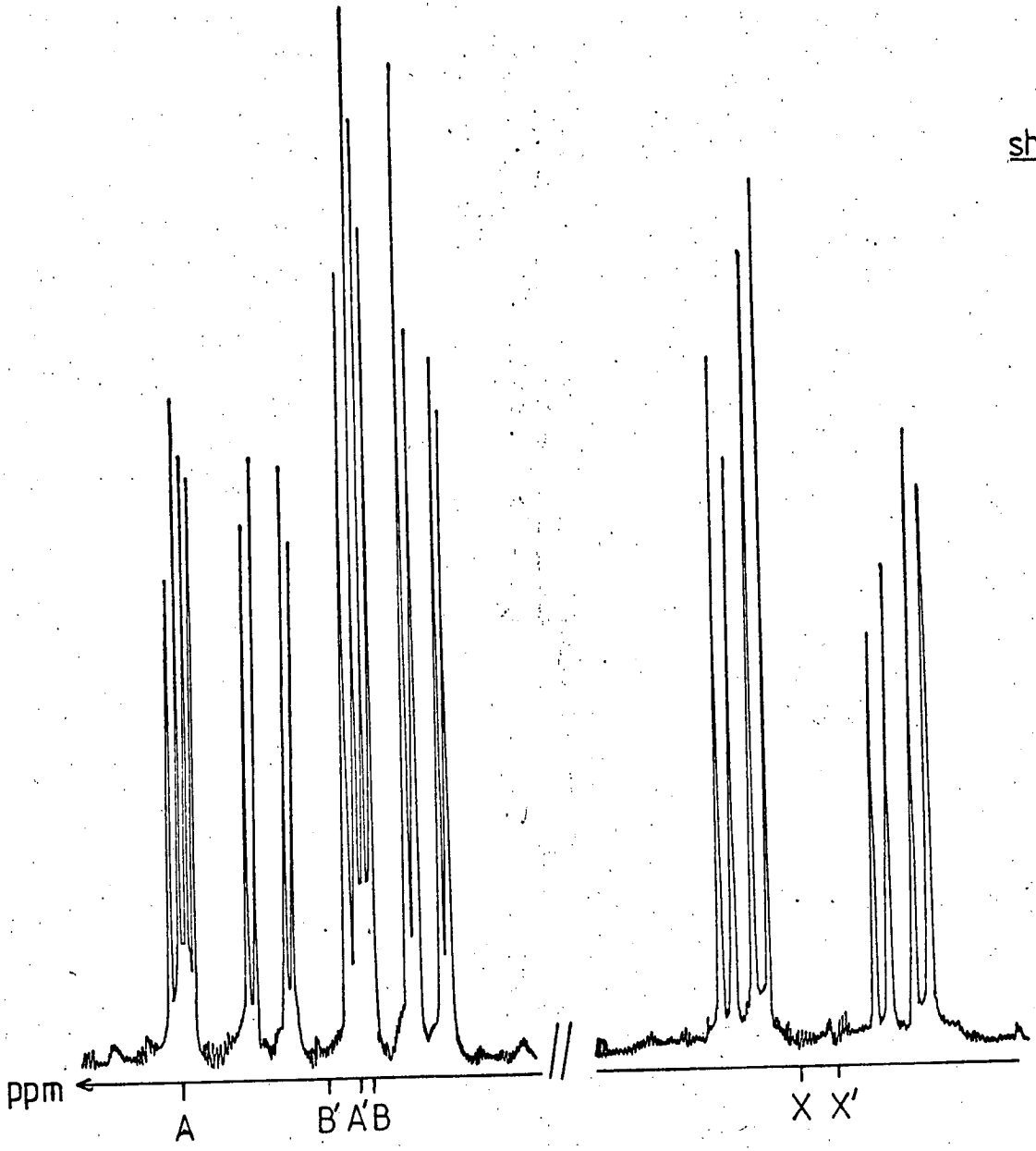
(i)	shift/p.p.m.		J(PP)/Hz	(ii)	shift/p.p.m.		J(PP)/Hz
A	74.99	AB	15.6	A′	66.24	AB′	15.0
B	65.24	AX	28.0	B′	67.61	AX′	26.2
X	5.11	BX	308.1	X′	3.35	BX′	318.6

The A and B resonances in each pattern are assigned to the two phosphorus atoms of the chelated etdiphos group, while the X resonance arises from the single PMe_2Ph group. The sizes of the coupling constants indicate that the PMe_2Ph group is coordinated trans to the B phosphorus atom of the etdiphos, giving rise to the largest coupling constant in each case; the two structures (32a) and (32b) are proposed, and (32b) has been confirmed by X-ray crystallography. If we assume that the



(32)

etdiphos phosphorus trans to oxygen (32a) will have a larger chemical shift than that trans to sulphur (32b) (see discussion of mer-$Ru(PhCOS)_2(PMe_2Ph)_3$ in Chapter 5), then spectrum (i), above, can



shifts: A 74·99 ppm A' 66·24 ppm
B 65·24 ppm B' 67·61 ppm
X 5·11 ppm X' 3·35 ppm

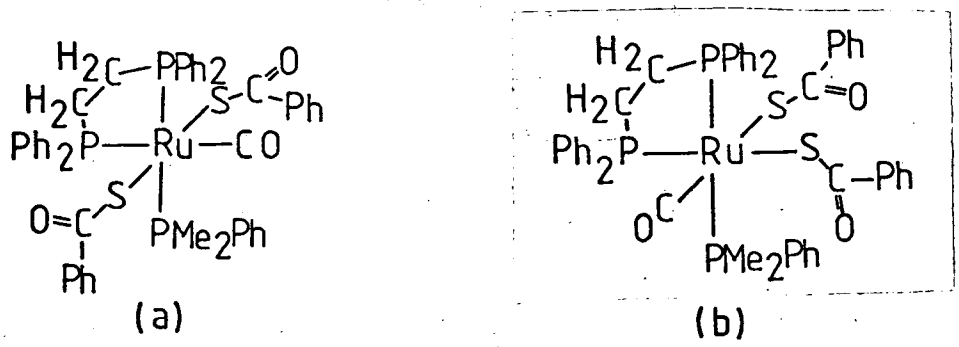
FIGURE 4.2 $^{31}P-\{^1H\}$-nmr spectrum of $Ru(PhCOS)_2(PMe_2Ph)(etdiphos)$

assigned to isomer (32a) and spectrum (ii), where the difference in shift between the etdiphos phosphorus atoms is much less, to isomer (32b).

When $Ru(PhCOS)_2(PMe_2Ph)$(etdiphos) was treated with carbon monoxide, a product was obtained which has one carbonyl stretching mode in the i.r. spectrum at 1990 cm^{-1}, and one new $\nu_{(CO)(acid)}$ band at 1560 cm^{-1}, together with the $\nu_{(CO)(acid)}$ bands at 1460 and 1545 cm^{-1} which were observed for the starting material. In the $^{31}P-\{^1H\}$-n.m.r. spectrum, the two ABX patterns arising from the isomers of $Ru(PhCOS)_2(PMe_2Ph)$-(etdiphos) are observed in the same relative proportions as before, but the strongest pattern in the spectrum, approximately three times more intense than either of those from the starting material, is a third ABX pattern:

	shift/p.p.m.		J(PP)/Hz
A	34.26	AB	19.5
B	52.66	AX	31.7
X	-4.88	BX	276.9

Clearly, the arrangement of phosphorus atoms is the same as in the starting material, and structure (33a) or (33b) is proposed for the CO adduct. The difference of almost 20 p.p.m. between the chemical shifts of the two



(33)

etdiphos phosphorus atoms suggests that the structure (33a), where the phosphorus atoms are trans to carbon and sulphur, is the more likely.

This isomer would be formed by cleavage of the Ru-O bond in isomer (32a) of the starting material, and it seems a reasonable suggestion since an Ru-O bond *trans* to phosphorus, as in (32a), would be expected to be more labile than one *trans* to sulphur, as in (32b). The carbonylation of $Ru(PhCOS)_2(PMe_2Ph)$(etdiphos) is by no means facile, as several hours refluxing in ethanol under carbon monoxide does not take the reaction to completion, and this is probably for simple steric reasons, as the coordination sphere of $Ru(PhCOS)_2(PMe_2Ph)$(etdiphos) is already extremely sterically crowded. However, none of this explains why *both* isomers of the starting material are still present after the carbonylation reaction, and in almost equal amounts. The presence of only one isomer of the carbonylated product suggests *either* that the two isomers of the starting material are in a dynamic equilibrium in refluxing ethanol solution, so that selective carbonylation of one isomer will always leave an isomeric mixture of the starting material, *or* that the products formed by the carbonylation of both isomers of $Ru(PhCOS)_2(PMe_2Ph)$(etdiphos) then rearrange to give only one form of $Ru(PhCOS)_2(PMe_2Ph)$(etdiphos)(CO). Although the $^{31}P-\{^1H\}$-n.m.r. spectrum of $Ru(PhCOS)_2(PMe_2Ph)$(etdiphos) shows no significant change when the temperature of the $CDC\ell_3$ solution is raised to 323K, the isomers of the complex may equilibrate in refluxing ethanol (*ca* 350K) by a solvent-assisted mechanism and, as the proportions of the two isomers do not vary appreciably from sample to sample, this seems the more likely explanation.

In order to elucidate the unexpected composition and stereochemistry of $Ru(PhCOS)_2(PMe_2Ph)$(etdiphos), an X-ray structure analysis was undertaken using crystals grown by slow evaporation from methanol.

4(iii) Determination of the Crystal Structure of $Ru(PhCOS)_2(PMe_2Ph)(etdiphos)$

The crystals of $Ru(PhCOS)_2(PMe_2Ph)(etdiphos).MeOH$ recrystallised from methanol solution were yellow-brown in colour and flat, with fairly well developed faces. Preliminary precession and Weissenberg photographs indicated that the crystals diffracted adequately, though not well enough to give a high-resolution structure, and were triclinic with cell dimensions:

a	= 10.01(1)Å	α	= 75.2(5)°
b	= 14.70(1)Å	β	= 83.6(5)°
c	= 18.52(1)Å	γ	= 73.5(5)°

(Standard deviations are estimated)

The photographs exhibited no systematic absences and the space group was assumed to be $P\bar{1}$ (n° 2), a centric space group which has two equivalent positions in the unit cell. Two molecules of $Ru(PhCOS)_2(PMe_2Ph)$-(etdiphos).MeOH, in a cell of the given dimensions, give a calculated density of 1.24g cm^{-3}, which compares reasonably well with the value of 1.27g cm^{-3} measured by flotation using water and saturated sodium bromide solution.

A crystal was then mounted about the c axis, aligned correctly using oscillation photographs, and transferred to a Stoe Stadi-2 two-circle automatic diffractometer. Data were collected using CuK_{α} radiation over one half of the reciprocal lattice ($hk\ell$, $\bar{h}k\ell$, $h\bar{k}\ell$ and $\bar{h}\bar{k}\ell$ reflections) out to $\theta = 40°$; due to the poor quality of the crystals, only 1274 of the 1640 reflections measured could be treated as observed. After data reduction, including the application of Lorentz and polarisation factors, but no absorption corrections, a Patterson map was calculated

using the SHELX program package[119]. There are two equivalent positions in the space group $P\bar{1}$, (x, y, z) and (-x, -y, -z), giving a general point in the Patterson map at (2x, 2y, 2z) and symmetry-related positions, and this peak was identified in the calculated map as

(2x, 2y, 2z) at (.4926, .2054, .4449)

giving (x, y, z) at (.2463, .1027, .2224) .

The ruthenium atom was given these coordinates, and a difference Fourier map was calculated using the XRAY76 program package[120] in which six atoms octahedrally coordinated to the ruthenium were located. The seven-atom fragment was then refined, with all the coordinated atoms treated as phosphorus, and individual isotropic temperature factors assigned to each. After two cycles of least-squares refinement, the temperature factor associated with one of the coordinated atoms had increased to almost three times the value originally assigned ($U = 0.05 Å^2$) and this atom was tentatively identified as the coordinated oxygen of a chelated monothiobenzoate group. A difference Fourier map based on the refined positions of the Ru and coordinated atoms revealed poorly-resolved peaks identifiable as carbon atoms bridging the oxygen and sulphur of the chelated monothiobenzoate group and connecting the two phosphorus atoms of the etdiphos group. Three carbon-atom peaks associated with the PMe_2Ph phosphorus and one close to the sulphur of the unidentate monothiobenzoate group enabled these ligands to be identified. A subsequent difference Fourier map contained broad, unresolved areas of electron density indicating the position of phenyl rings bonded to the phosphorus atoms and the carbon atoms of the acid groups, and over a series of difference Fourier maps, idealised phenyl rings were fitted to the electron density areas in turn, beginning with the best resolved. After all the phenyl rings and the uncoordinated acid oxygen had been added,

the resulting difference Fourier map was free from major peaks of electron density, but the R-factor was still high, ca 0.34. Least-squares refinement was begun with the idealised phenyl rings being refined as rigid bodies, and after two cycles a difference Fourier map revealed two additional peaks which were interpreted as the oxygen and carbon atoms of a molecule of methanol, with the oxygen hydrogen-bonded to the uncoordinated oxygen of the monothiobenzoate group. Further refinement led to improvement of the bond distances and angles in all the ligands, except the chelated monothiobenzoate group. The bridging carbon in this ligand, C35, tended to refine so as to make the C-O and C-S distances, and the O-C-S angle, implausible, and it proved impossible to obtain a meaningful temperature factor for this atom. The temperature factors for the ruthenium and phosphorus atoms, and the sulphur of the unidentate monothiobenzoate group, were given individual anisotropic temperature factors, with isotropic temperature factors for all the other atoms. In particular, the sulphur atom of the chelated acid group was given an isotropic temperature factor as its anisotropic parameters were strongly coupled with the temperature factor of C35, and refinement of the anisotropic values led to further complications in the refinement of parameters for the bridging carbon.

Further refinement took the R-factor to 0.163 and at this stage, an analysis of the reflections in terms of $\sin\theta$ and $|F_{obs}|$ values revealed that agreement was bad for reflections having $|F_{obs}| < 32.0$. These weak reflections, which were clearly very poorly determined, were eliminated and refinement was continued using the remaining 1094 reflections, with unit weights for all reflections. The refinement effectively converged with $R = 0.15$. At this stage, no parameter was shifting by more than one standard deviation and, given the restricted

size and poor quality of the data set, it was clear that no further improvement in the structure was possible. A final difference Fourier map showed no significant peaks of electron density, although the general noise level remained high, and further attempts to refine the structure were abandoned. Structure factors and tables of atomic positional and thermal parameters are given in Tables 4.3 and 4.4.

4(iv) Discussion of the Structure

Bond distances and angles are given in Tables 4.5, and a view of the molecule, and its crystal packing are shown in Figure 4.3. The poor resolution of the structure, reflected in the large standard deviations in both distances and angles, makes a detailed discussion, for example comparing ligand dimensions with those found in previous structures, meaningless. However, one or two points can be made.

The coordination about the ruthenium is in the form of a distorted octahedron, with the largest deviation from ideal geometry arising from the small ligand bite of the chelated monothiobenzoate group (S1-O1 = 2.54Å, S1-Ru-O1 = 67.2°). That much is clear, although the geometry of the chelated acid group is not well determined. The unsatisfactory behaviour of the bridging carbon atom during refinement has already been mentioned, and in the structures discussed in previous chapters, especially that of $Ru(PhCOS)_2(PMe_2Ph)_2(HNCMeCH_2CMe_2NH_2)$, the position of the thiocarboxy-carbon atom in the monothiobenzoate groups has tended to be among the worst determined in the structure. This is reflected, for instance, in the significant differences which were found between comparable C-O and C-S distances in the monothiobenzoate groups of $Ru(PhCOS)_2(PMe_2Ph)_2(NHCMeCH_2CMe_2NH_2)$.

The uncoordinated oxygen atom of the unidentate monothiobenzoate

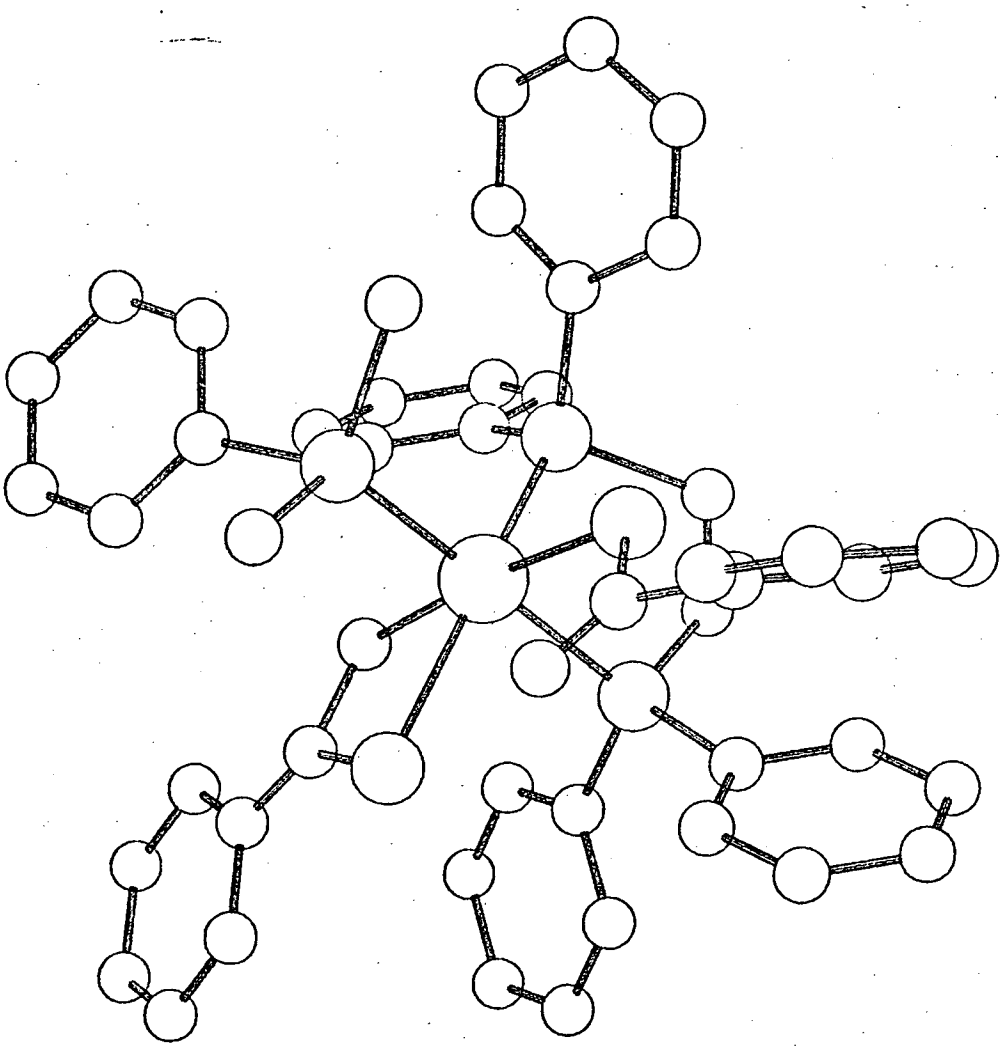


FIGURE 4.3 Molecular structure of $Ru(PhCOS)_2(PMe_2Ph)(etdiphos)$

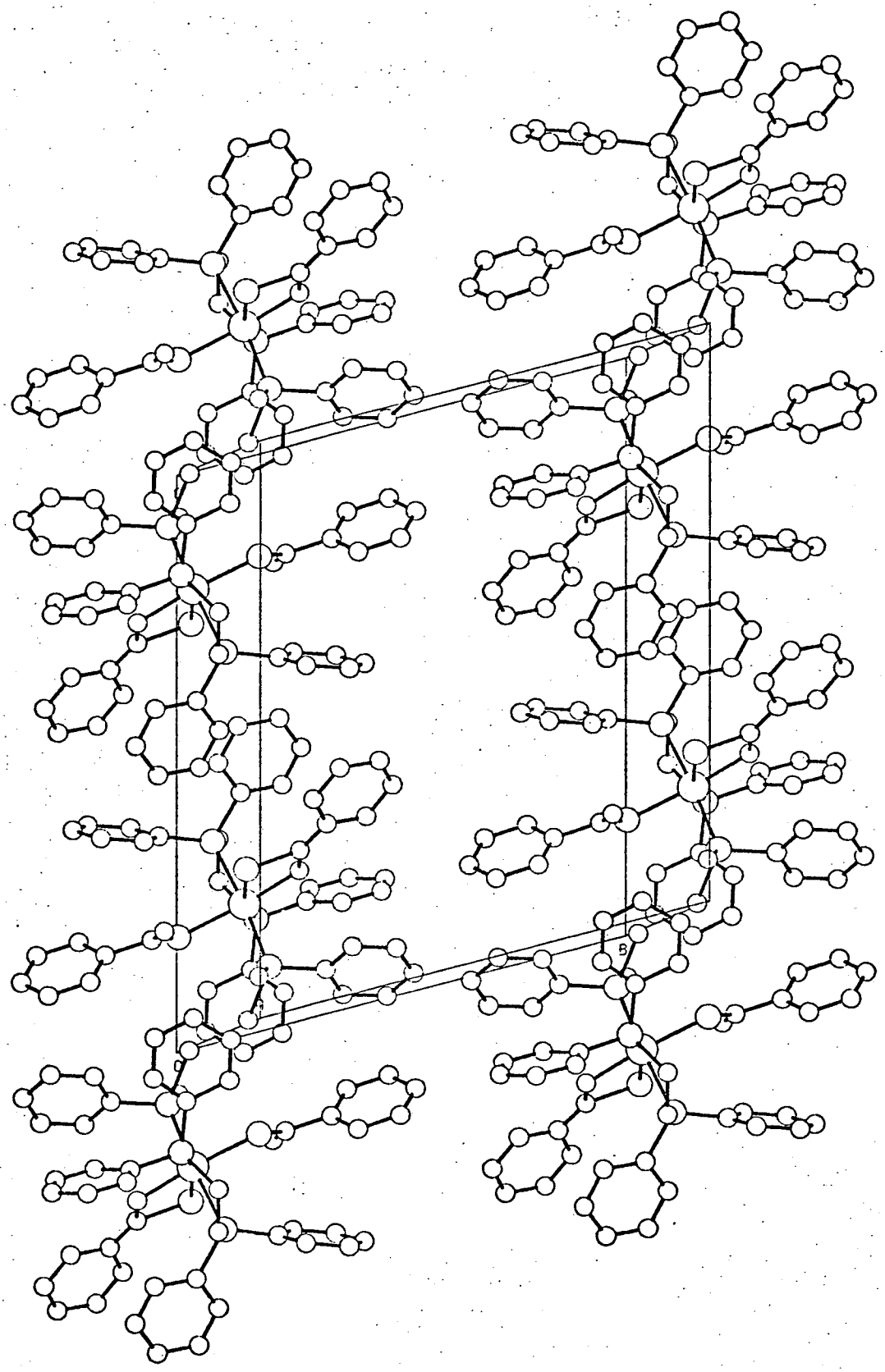


FIGURE 4.3 Crystal packing of $Ru(PhCOS)_2(PMe_2Ph)_2$(etdiphos)

group is hydrogen-bonded to a molecule of the methanol solvent from which the compound was recrystallised (O-O ca 3.0Å), and this type of hydrogen bonding may account for the fairly low value of the $\nu_{(CO)}$ mode in the i.r. spectrum of the complex. The unidentate monothiobenzoate group is slightly twisted from its preferred coordination geometry (Ru-S2-C42-O2 = 8°), probably due to the effect of the hydrogen bonding, and to the crowding of bulky ligands into the octahedral coordination sphere.

Experimental

Experimental details are as given in the Experimental Section of Chapter 2. Bis(diphenylphosphine)methane was obtained by a method similar to that of Isslieb and Müller[121], and bis(diphenylphosphino)ethane by the method of Chatt and Hart[122,123].

Tris(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II)-(bis(diphenylphosphino)methane)

The compounds $Ru(PhCOS)_2(PMe_2Ph)_2$ (0.1g) and $Ph_2PCH_2PPh_2$ (0.06g) were refluxed in ethanol (50 ml) for 2h. The volume of the solution was reduced and on cooling the yellow product was filtered off and recrystallised from ethanol (0.06g, 38%), m.p. 119-122°C (Found: C, 65.64; H, 5.17. Calc. for $C_{63}H_{65}O_2P_5RuS_2$: C, 64.40; H, 5.54%) Mull i.r. spectrum: $\nu_{(CO)}$ 1530-1560 cm^{-1}, $\nu_{(CS)}$ 930, 960 cm^{-1}.

(Bis(diphenylphosphino)ethane)(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II)

The compounds $Ru(PhCOS)_2(PMe_2Ph)_2$ (0.1g) and $Ph_2PC_2H_4PPh_2$ (0.06g) were refluxed in ethanol (50 ml) for 2h. The volume of the solution was reduced

and on cooling the yellow-brown product was filtered off and recrystallised from methanol (0.1g, 73%) m.p. 107-109°C (loss of solvent and decomp.) (Found: C, 63.88, H, 5.14; M($(CH_3)_2CO$)896. Calc. for $C_{49}H_{41}O_3P_3RuS_2$: C, 62.35; H, 5.20; M 911) Mull i.r. spectrum: $\nu_{(CO)}$ 1460, 1545 cm^{-1}.

(Bis(diphenylphosphino)ethane)(carbonyl)(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II)

The compound $Ru(PhCOS)_2(PMe_2Ph)$(etdiphos) (0.1g) was refluxed in ethanol (50 ml) under an atmosphere of CO gas for 2h. The volume of the solution was reduced and on cooling the yellow product was filtered off (0.08g, 78%) m.p. 104-107°C (loss of solvent) (Found: C, 64.07; H, 4.91. Calc. for $C_{49}H_{48}O_3P_3RuS_2$: C, 62.62; H, 4.79%) Mull i.r. spectrum: $\nu_{(CO)(carbonyl)}$ 1990 cm^{-1}, $\nu_{(CO)(acid)}$ 1460, 1545 and 1560 cm^{-1}.

TABLE 4.1 (see also Figure 4.1)

^{1}H-n.m.r. data in $CDC\ell_3$ for a ruthenium(II) monothiobenzoate complex with a bidentate phosphorus-donor Lewis Base (at 300K)

	δ ± 0.01 p.p.m.	
Complex	methyl of phosphine	other
$Ru(PhCOS)_2(PMe_2Ph)$(etdiphos)	1.25 (dd)	2.80 - 3.20(u)[a]
	1.46 (dd)	6.80 - 7.50[b]
	1.78 (dd)	

dd = doublet of doublets u = unresolved

[a] ethylenic protons of $Ph_2PC_2H_4PPh_2$ ligand

[b] phenyl resonances.

TABLE 4.2

$^{31}P-\{^{1}H\}$-n.m.r. data for some ruthenium(II) monothiobenzoate complexes with bidentate phosphorus-donor Lewis bases. (All at 300K)

Complex		δ ± 0.01 p.p.m.		J(PP)/Hz
$Ru(PhCOS)_2(PMe_2Ph)(etdiphos)$[b]	A	74.99	AB	15.6
	B'	67.61	A'B'	15.0
	B	65.82	AX	28.0
	A'	66.24	A'X'	26.2
	X	5.11	BX	308.1
	X'	3.35	B'X'	318.6
$Ru(PhCOS)_2(PMe_2Ph)(etdiphos)(CO)$	B	52.66	AB	19.5
	A	34.26	AX	31.7
	X	-4.88	BX	276.9

[a] ^{31}P chemical shift quoted in p.p.m. to high frequency of 85% H_3PO_4

[b] See also Figure 4.2.

Table 4.3: Structure factors for $Ru(PhCOS)_2(PMe_2Ph)(etdiphos).MeOH$

Columns are h, $10|F_o|$, $10|F_c|$.

H,0,0

2	1022	1075
4	966	888

H,1,0

-5	211	236
-2	926	1026
-1	775	747
2	207	338
4	556	558
5	382	367

H,2,0

-5	365	244
-2	396	491
-1	1213	1241
0	579	727
1	765	902
4	383	358
5	233	345

H,3,0

-1	283	358
0	836	786
1	1203	1166
2	338	373
4	183	237
5	224	175

H,4,0

-2	199	43
-1	189	185
0	785	830
1	254	127
2	285	155
4	324	303

H,5,0

-2	472	530
-1	251	212
0	876	861
2	417	406
4	208	187

H,6,0

-4	249	244
-2	649	648
0	819	862
1	740	589
4	434	337

H,7,0

-1	300	376
1	307	280
5	260	308

H,8,0

-2	172	270
-1	629	609
2	164	263

H,9,0

-2	423	390
-1	266	226
2	417	437

H,10,0

2	178	164

H,11,0

4	179	259

H,-10,1

-2	421	342
-1	243	117
1	192	108

H,-9,1

0	375	406
2	269	130

H,-8,1

-2	219	246
0	496	533
1	232	319
2	203	395

H,-7,1

-5	245	60
-4	302	210
-2	479	470
2	659	733
4	574	668

H,-6,1

-2	416	434
1	239	214
2	700	684
4	447	599

H,-5,1

-2	669	674
-1	214	122
0	450	416
2	250	88

H,-4,1

-5	455	599
-4	233	207
-2	312	351
-1	425	397
1	501	459
2	232	70
5	179	202

H,-3,1

-4	208	243
-1	230	43
0	916	861
2	446	450
4	851	765

H,-2,1

-5	236	184
-4	204	208
0	941	1138
1	436	481
2	1107	1162
4	1087	1012

H,-1,1

-5	428	455
-2	1450	1536
1	916	920
2	413	427
4	1042	998

H,0,1

-5	403	454
-4	270	275
-2	690	679
2	1178	1066
4	609	675
5	594	607

H,1,1

-4	569	545
-2	579	478
2	278	329
4	193	178
5	518	510

H,2,1

-5	330	216
-4	564	563
-2	285	311
-1	417	489
0	876	813
1	554	355
4	534	568

H,3,1

-5	219	223
-4	644	605
-2	926	891
-1	173	207
0	1122	1272
1	187	210
2	170	166
4	197	259

H,4,1

-1	468	415
0	780	737
1	896	1035
5	271	228

H,5,1

-4	198	298
-2	210	152
-1	417	396
0	222	264
1	1268	1225
2	223	230
5	464	755

H,6,1

-5	508	38
-2	609	568
-1	634	717
0	404	389
1	1560	1547
2	831	842
4	188	124
5	297	361

H,7,1

-4	424	467
-2	946	938
-1	513	441
0	470	559

H,7,1

1	280	180
2	503	553
4	224	136

H,8,1

-4	486	563
-2	866	824
0	574	631
1	292	316
2	347	272

H,9,1

-2	513	431
-1	167	193
0	383	369
4	249	171

H,11,1

2	246	222

H,-10,2

-2	166	116

H,-9,2

-5	261	59
-4	163	192
-2	549	413
0	220	243

H,-8,2

-2	685	608
2	338	398

H,-7,2

-5	440	454
-1	569	493
1	245	216
2	443	428

H,-6,2

-5	271	311
-4	285	413
-1	309	294
0	419	516
4	304	348

H,-5,2

-5	165	150
-4	276	202
-1	404	238
2	260	192

H,-4,2

-2	425	410
-1	267	363
0	371	356
4	332	416

H,-3,2

-5	343	423
-2	375	294
-1	337	273
0	298	227
1	176	43
2	325	418
4	594	615
5	381	316

H,-2,2

-5	438	391
-2	619	589
-1	396	404
0	188	177
1	1485	1290
2	452	351
4	236	176
5	836	787

H,-1,2

-5	258	214
-4	405	370
-1	921	1171
0	416	397
1	780	799
2	171	137
4	669	636
5	594	529

H,0,2

-4	876	841
-1	349	313
1	231	103
2	1097	1067
4	1480	1256
5	564	548

H,1,2

-4	579	464
-2	246	71
-1	710	509
0	1107	1065
2	1208	1065
4	1002	969

H,2,2

-5	199	296
-4	289	232
-1	669	890
1	1042	1116
2	358	468
4	513	377
5	371	457

H,3,2

-2	286	295
0	172	85
2	255	262

H,4,2

-4	385	392
0	836	794
2	169	75
4	256	217
5	166	195

H,5,2

-4	508	449
-3	272	336
-2	393	421
-1	255	196
0	770	778
2	549	436
4	334	269

H,6,2

-4	186	240
-3	508	591
-2	485	572
-1	230	281
0	1082	1065
1	700	785
2	1032	968
4	523	582

H,7,2

-3	745	771
-2	436	495
-1	705	630
0	464	462

H,8,2

-3	589	610
-1	805	776
1	371	489

H,9,2

-2	305	299
-1	431	461
4	276	238

H,10,2

0	177	105

H,11,2

2	228	107

H,-10,3

-1	218	354

H,-9,3

-2	186	65
-1	518	346
0	225	308
1	443	351

H,-8,3

-4	202	286
-2	549	482
-1	234	230
0	161	270
1	429	381

H,-7,3

-2	1278	1269
1	344	263

H,-6,3

-4	455	452
-3	247	188
-2	956	912
2	584	582

H,-5,3

-5	270	330
-3	494	452
-2	288	256

H,-5,3

-1	173	50
1	313	149
4	224	197

H,-4,3

-5	172	337
-3	192	195
-1	320	312
5	385	257

H,-3,3

-5	609	636
-3	204	156
-2	308	414
0	351	165
1	251	136
2	755	680
4	649	614

H,-2,3

-4	276	203
-1	841	967
0	382	520
2	511	866
4	736	782

H,-1,3

-5	765	693
-4	664	514
-3	254	143
-2	1278	1251
-1	311	506
0	217	162
1	425	561
2	201	317
4	1173	1234
5	604	653

H,0,3

-5	1158	1020
-4	936	790
-3	203	192
-2	594	569
-1	354	333
0	465	520
4	755	597
5	644	721

H,1,3

-5	736	680

H,-3,3

-3	169	95
-1	165	51
0	241	228
1	1213	1367
2	644	734

H,2,3

-5	461	356
-3	268	327
-1	1369	1166
0	335	431
1	1309	1186
4	503	427
5	236	158

H,3,3

-2	336	347
-1	301	185
0	725	654
1	363	362
2	401	255
4	614	713

H,4,3

-4	240	120
-3	237	233
-2	249	172
0	356	467
1	725	764
2	326	379
4	324	465

H,5,3

-3	491	579
1	1238	1307
2	173	101
4	317	339
5	240	301

H,6,3

-4	403	457
-3	220	218
0	444	463
1	1485	1428
4	241	128

H,7,3

-4	145	283
-2	265	318
-1	966	965
0	392	444
1	740	679

H,-5,4

-5	391	432
-3	289	208

2	353	331
4	167	285

H,8,3

-2	584	638
-1	401	420
0	609	598
2	485	450

H,9,3

-2	579	615
0	274	298
2	202	157

H,10,3

1	349	264
2	184	293

H,11,3

1	212	209

H,-9,4

-4	249	311
-2	539	582
0	564	458

H,-8,4

-4	589	308
-2	750	730
0	328	321

H,-7,4

-3	659	664
-3	659	664
-2	539	411
-1	584	568
1	383	304

H,-6,4

-4	321	110
-3	745	705
-2	249	328
-1	831	797
1	360	453
2	375	322

H,-5,4

-5	391	432
-3	289	208

-2	649	617
-1	420	307

H,-4,4

-3	207	159
-2	755	817
-1	264	306
0	304	315
4	281	164

H,-3,4

-5	457	382
-4	492	593
-3	629	669
-2	501	498
-1	284	299
1	283	226
2	374	444
5	203	225

H,-2,4

-5	1294	1123
-4	836	418
-3	489	587
-2	1052	975
0	258	297
1	270	268
2	554	367
5	500	456

H,-1,4

-5	1742	1473
-4	233	154
-3	268	358
-2	432	429
0	1102	993
5	513	493

H,0,4

-4	760	880
-3	403	455
-2	2023	1871
-1	174	415
0	836	920
1	966	1030
2	931	769
4	1102	1045
5	316	345

H,1,4

-4	1117	1156

H,1,4

-2	851	816
-1	252	278
0	460	542
1	669	583
2	406	413
4	750	702

H,2,4

-5	679	617
-4	664	575
-2	173	141
1	1646	1389
2	518	534
4	356	261
5	243	265

H,3,4

-5	679	577
-4	262	93
-3	326	267
-1	450	524
0	564	511
2	523	573
5	359	389

H,4,4

-5	388	322
-4	453	437
0	460	488
1	559	477
4	451	543
5	413	468

H,5,4

-4	434	456
-2	210	70
-1	260	276
1	453	414
2	389	364
4	316	208

H,6,4

-4	460	450
-3	353	404
-2	448	412
-1	345	390
0	449	467
1	231	343
2	256	671
4	256	371

H,7,4

-3	379	407
-2	725	726
0	245	291
1	624	616
2	851	837
4	204	424

H,8,4

-3	390	296
-2	306	328
-1	493	450
0	332	359
1	926	998

H,9,4

-1	483	540
1	282	382

H,10,4

-1	319	277
2	298	407

H,11,4

2	209	93

H,-9,5

-3	266	219
-1	452	433

H,-8,5

-1	455	402
1	851	873

H,-7,5

-3	338	334
-2	579	627
-1	184	187
0	355	382

H,-6,5

-5	185	73
-4	232	129
-3	208	232
-2	856	761
-1	247	255
0	471	462
2	569	623
4	182	153

H,-5,5

-3	487	406
-2	1017	893

H,-4,5

-5	209	251
-3	391	353
-2	438	379
-1	262	289
2	275	280
4	261	201

H,-3,5

-5	523	523
-4	390	476
-2	644	714
-1	936	1001
1	437	468
2	365	324
4	258	157

H,-2,5

-5	207	265
-4	765	798
-1	679	733
0	352	378
1	491	440
2	371	317
4	518	614
5	302	321

H,-1,5

-5	445	365
-4	326	381
-2	1550	1626
-1	500	512
0	484	579
1	931	821
2	271	92
4	725	687

H,0,5

-5	1112	973
-4	695	763
-3	720	722
-2	1198	1215
-1	1218	1217
0	1837	1674
1	440	398
2	760	745
4	484	470

H,1,5

-5	1379	1173
-3	921	934
-2	387	339
0	415	337
1	775	828
2	901	933
4	195	39

H,2,5

-5	1097	909
-3	285	283
0	283	293
1	360	243
5	406	547

H,3,5

-5	276	279
-4	319	332
-1	472	440
1	196	49
2	312	269
4	513	625

H,4,5

-4	695	701
-3	564	447
-2	289	190
0	654	719
1	184	107
2	644	574
4	695	1026

H,5,5

-5	441	560
-4	371	432
-3	589	593
-2	353	311
-1	458	488
0	549	592
1	685	743
2	690	668
4	274	404
5	395	621

H,6,5

-3	554	577
-2	330	305
-1	332	361
1	281	909

Table 4.3 continued

H,6,5

4	270	252
5	246	402

H,7,5

-4	401	376
-3	395	368
-1	450	373
0	352	471
1	405	398

H,8,5

-4	198	221
0	554	578
2	467	453
4	174	211

H,9,5

-2	251	200
-1	309	210
0	417	458
2	341	321

H,10,5

1	193	310
2	300	53
4	170	141
5	209	226

H,-8,6

-2	432	400
0	443	505

H,-7,6

-4	224	268
-2	341	369
1	381	356
2	539	523

H,-6,6

-4	224	90
-2	399	426
-1	490	498
1	382	402

H,-5,6

-5	161	112
-3	492	530
-1	569	630

0	324	255
1	395	458
2	260	212

H,-4,6

-5	168	145
-2	654	667
-1	452	505
0	369	319
1	554	601

H,-3,6

-5	194	35
-4	286	26
-3	156	334
-2	871	904
0	478	583
2	644	639
4	332	326
5	287	111

H,-2,6

-5	554	449
-2	1352	1152
-1	1233	1313
0	335	359
1	288	362
2	936	839
5	222	124

H,-1,6

-5	609	478
-3	404	578
-2	166	139
-1	1616	1542
1	291	315
2	363	351

H,0,6

-6	470	541
-5	695	562
-4	224	79
-3	810	910
-2	294	479
-1	1294	1311
0	574	454
1	644	679
2	413	322
4	288	230

H,1,6

-6	584	472

-5	457	480
-4	710	771
-3	584	577
-2	655	680
-1	579	458
0	599	651
1	1092	934
2	685	496
4	473	602
5	179	252

H,2,6

-6	423	283
-4	740	733
-3	393	384
-2	389	378
-1	518	491
0	534	677
4	387	444

H,3,6

-5	629	652
-4	378	500
-2	523	528
-1	406	307
1	318	140
2	175	88
4	240	156

H,4,6

-5	730	722
-4	297	300
0	210	124
1	200	246
2	434	395
4	357	350
5	425	562

H,5,6

-3	279	351
-1	381	415
0	574	523
1	391	170
2	248	210
4	382	580

H,6,6

-4	740	821
-3	284	308
-2	421	423
0	730	754
1	359	338
2	831	689

4	261	499

H,7,6

-4	270	403
-3	356	269
-2	445	427
0	187	284
1	252	284
2	390	215
4	195	473

H,8,6

-3	397	367
-1	230	85
1	298	275
2	266	125

H,9,6

0	189	4
1	268	330

H,10,6

5	170	87

H,-8,7

-3	224	326
0	234	124

H,-7,7

-3	292	227
1	513	572

H,-6,7

-2	165	57
-1	244	292
0	171	173
2	534	464

H,-5,7

-2	284	364
1	235	176
2	529	430

H,-4,7

-5	162	249
-2	549	586
-1	487	471
0	478	476

H,-4,7

1	584	629
2	302	344

H,-3,7

-5	171	77
-1	705	728
0	166	75
1	715	615

H,-2,7

-6	179	231
-4	189	110
-3	659	637
-2	1007	997
-1	805	777
0	790	865
1	679	608
2	336	247
4	441	425

H,-1,7

-6	220	162
-4	276	347
-3	216	115
-2	1107	1215
0	820	910
1	346	298
2	441	377
4	250	227

H,0,7

-4	614	653
-2	705	721
0	966	1087
1	286	250
2	381	334
4	330	232
5	474	327

H,1,7

-4	594	628
-2	649	609
-1	831	899
0	326	365
2	181	125
4	327	315

H,2,7

-5	469	423
-3	911	966

-1	534	672
1	215	150
2	760	765
5	187	120

H,3,7

-5	181	261
-4	372	501
-1	354	399
0	518	512
1	599	597
2	421	369
4	367	485

H,4,7

-5	218	117
-4	639	752
-2	178	80
-1	228	234
0	554	540
1	169	318
2	179	73
4	306	504

H,5,7

-4	481	543
-2	426	361
-1	463	432
0	398	396
2	337	351
4	204	231

H,6,7

-4	262	218
-3	381	471
-2	399	382
-1	502	418
0	217	172
1	401	425
2	370	285

H,7,7

-4	184	124
-3	745	750
-2	221	219
-1	639	549
0	187	191
2	341	239

H,8,7

1	253	301

H,10,7

0	212	41
1	249	206
4	196	276

H,11,7

4	219	227

H,-7,8

0	325	253

H,-6,8

2	378	312

H,-5,8

1	326	376
2	296	198

H,-4,8

0	322	347
1	400	399

H,-3,8

-3	221	206
-2	705	686
-1	235	185
0	387	467
2	740	691
4	238	339

H,-2,8

-2	589	672
-1	569	621
0	336	383
2	785	752
4	496	468

H,-1,8

-5	168	203
-4	356	412
-3	836	836
-1	881	890
1	513	578
2	290	294
4	257	188

H,0,8

-5	323	358

-5	323	358
-3	443	464
-2	281	344
-1	775	731
1	343	308
2	374	514
5	238	126

H,1,8

-3	359	440
-1	442	415
0	740	657
1	710	654

H,2,8

-3	282	293
-2	765	861
-1	319	311
0	496	465
1	685	501

H,3,8

-5	356	395
-4	241	338
-2	574	612
-1	476	374
1	323	270
2	202	96

H,4,8

-4	194	42
-3	231	363
-1	584	563
1	300	280

H,5,8

-3	564	653
-1	625	662
1	619	548

H,6,8

-4	559	706
-1	388	394
0	453	443
1	450	530

H,7,8

-4	644	663
-3	375	326
-2	705	618

H,7,8

0	341	378
1	277	239

H,8,8

-2	589	448
-1	218	282
1	192	251

H,9,8

1	237	82

H,-5,9

-4	176	146
0	205	131
2	360	400

H,-4,9

-2	180	213
0	187	262
1	371	443
2	358	319
4	224	324

H,-3,9

-5	170	64
-3	469	434
-1	353	450
1	609	624

H,-2,9

-3	564	572
-2	300	243
-1	710	689
1	624	540

H,-1,9

-5	241	218
-3	214	218
-2	478	523
-1	370	344
0	216	155
1	480	517
2	775	650

H,0,9

-4	355	323
-3	327	304
-2	523	645

0	379	715
1	472	493
2	941	929
4	310	352

H,1,9

-2	209	169
-1	333	346
0	518	605
1	180	62
4	223	154

H,2,9

-3	266	166
-2	405	315
-1	775	794
1	639	569
2	355	443

H,3,9

-3	265	299
-2	189	176
-1	831	808
0	390	385
1	831	744
4	236	133

H,4,9

-4	589	522
-2	356	741
-1	344	279
0	649	721
1	765	651
2	374	293
4	266	377

H,5,9

-4	446	486
-2	1087	888
-1	227	191
2	460	406

H,6,9

-4	244	372
-2	710	662
-1	534	450
0	354	256
2	366	372
4	245	174

H,7,9

-3	518	598
-2	491	469
-1	539	542
1	203	365

H,8,9

5	190	54

H,9,9

-1	323	240
4	216	59

H,-5,10

-3	402	427
1	228	291

H,-4,10

2	380	277

H,-3,10

-3	361	275
-2	659	674
2	861	815

H,-2,10

-6	444	493
-2	690	744
2	805	757
4	217	392

H,-1,10

-6	351	400
-2	405	343
-1	177	248
0	391	385
1	497	424
2	599	511
4	338	265

H,0,10

-6	267	144
-2	207	175
-1	508	562
0	644	652
1	554	459
2	163	108

H,1,10

-2	477	467
-1	211	235
1	569	504
2	261	288
4	273	144
5	233	252

H,2,10

-4	254	95
-1	172	181
0	584	491
2	624	558

H,3,10

-3	201	83
-2	508	485
-1	534	389
0	876	885
2	976	889

H,4,10

-2	292	220
-1	861	771
0	513	509
2	465	477

H,5,10

-4	196	54
-3	534	575
-1	1017	891
1	800	836
2	196	82

H,6,10

-3	554	536
-1	664	513
0	569	562
1	365	458

H,7,10

-2	445	476
0	375	350

H,8,10

2	240	373

H,9,10

-1	304	264
4	209	130

H,-4,11

-3	162	269
-2	344	391
0	168	121

H,-3,11

-3	447	522
-1	181	313
1	244	233
2	389	414

H,-2,11

-3	518	545
-1	513	526
1	497	448

H,-1,11

-4	188	85
-3	321	282
1	292	232
2	314	374

H,0,11

-2	417	323
1	235	218
2	659	684

H,1,11

-4	284	413
1	304	370
2	391	436

H,2,11

-4	220	116
-2	197	139
-1	690	515
2	408	356

H,3,11

-3	227	185
-1	431	401
1	604	539

H,4,11

-2	277	301
0	240	196
1	654	616
2	190	205

H,5,11

0	639	652
1	276	207
2	437	418
5	229	361

H,6,11

-2	730	592
-1	321	329
0	449	425
1	208	36
2	317	424

H,7,11

-1	480	390
2	356	533

H,8,11

-1	518	466
1	266	195
2	195	248
4	269	374

H,9,11

0	240	221

H,-2,12

-3	276	49
2	508	518

H,-1,12

-4	285	434
-3	221	162
-2	325	389
0	285	188
1	240	243
2	451	456

H,0,12

0	190	258
1	220	43

H,1,12

0	327	331
1	254	180
4	227	164

H,2,12

-2	289	190
4	257	341

H,3,12

2	559	504

H,4,12

-1	252	182
0	380	284
2	416	501

H,5,12

-2	162	68
-1	468	437
0	298	299
2	331	537

H,6,12

-1	445	412
0	224	202
1	293	409
2	227	247

H,7,12

1	264	327
4	240	116

H,-2,13

1	379	335

H,-1,13

-1	476	473
1	286	209

H,0,13

-2	518	316
-1	286	348
0	201	98
2	391	384

H,1,13

-2	205	252

H,3,13

-1	220	202
1	215	132

H,4,13

0	225	152
2	285	189

H,5,13

0	181	290
2	164	298
4	288	217

H,7,13

1	231	88
2	181	226
4	263	69

H,1,14

-1	278	251

H,4,14

-1	212	159
0	247	251

H,5,14

0	163	160

TABLE 4.4

Atomic and thermal parameters ($\times 10^4$) for $Ru(PhCOS)_2(PMe_2Ph)(etdiphos)$

Estimated standard deviations are given in brackets.

Atom	x/a	y/b	z/c	$U(A^2)$
Ru	2457(7)	1041(4)	2213(3)	[a]
P1	171(20)	1733(13)	1960(10)	[a]
P2	1590(21)	498(14)	3461(9)	[a]
P3	3428(21)	1420(12)	1004(10)	[a]
S1	4749(23)	662(14)	2756(10)	783(70)
S2	2269(20)	-395(12)	1947(10)	[a]
O1	2776(44)	2224(25)	2538(18)	470(120)
O2	4800(66)	1179(34)	2056(25)	940(190)
C1	-328(68)	988(40)	3519(31)	520(200)
C2	-825(74)	1080(45)	2801(36)	680(230)
C27	2589(72)	1103(43)	185(32)	680(220)
C28	5347(73)	829(43)	832(32)	660(220)
C35	4116(54)	1987(30)	2855(22)	[b]
C42	3760(100)	-1266(53)	1986(37)	810(280)
C3	485	2988	2048	430(190)
C4	-1878	3326	2276	1100(290)
C5	-2424	4308	2303	900(240)
C6	-1578	4948	2103	550(200)
C7	-183	4611	1875	740(220)
C8	364	3631	1848	840(250)
C9	-566	1757	1117	420(180)
C10	-855	2547	583	970(260)
C11	-1378	2612	-103	1040(270)
C12	-1611	1789	-260	920(250)
C13	-1319	900	272	600(210)
C14	-795	833	959	480(200)
C15	2023	1041	4173	480(190)
C16	2804	397	4767	720(220)
C17	3207	759	5314	610(210)
C18	2825	1761	5270	790(230)
C19	2042	2405	4678	640(210)
C20	1642	2043	4130	310(170)
C21	2166	-812	3787	730(230)

TABLE 4.4 (Contd.)

Atom	x/a	y/b	z/c	U/A^{o2}
C22	1083	-1242	4080	1050(280)
C23	1360	-2258	4321	860(240)
C24	2722	-2844	4271	640(210)
C25	3806	-2413	3978	720(220)
C26	3527	-1397	3734	620(220)
C29	3523	2681	688	450(190)
C30	4390	3114	947	700(220)
C31	4202	4126	722	830(240)
C32	3147	4703	238	600(210)
C33	2281	4271	-23	940(250)
C34	2468	3259	201	320(160)
C36	4669	2489	3184	1000(260)
C37	5799	1984	3638	750(230)
C38	6323	2473	4050	710(220)
C39	5714	3465	4010	990(260)
C40	4584	3970	3556	980(270)
C41	40 1	3480	3143	780(230)
C43	3626	-2278	1938	790(240)
C44	4661	-2810	1519	560(200)
C45	4621	-3739	1472	560(200)
C46	3547	-4135	1844	640(210)
C47	2514	-3604	2263	790(240)
C48	2553	-2674	2308	630(210)
O3	7495(93)	-2353(59)	2774(42)	2400(350)
C49	8575(135)	-1755(80)	2198(61)	2400(490)

Anisotropic temperature factors $(\times 10^4)/A^{o2}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	620(50)	570(40)	450(40)	240(30)	250(30)	10(30)
P1	420(170)	670(150)	570(140)	-60(120)	10(120)	-70(110)
P2	580(200)	850(170)	440(140)	240(140)	340(130)	-170(120)
P3	580(190)	440(130)	780(150)	110(130)	230(130)	-120(120)
S2	590(180)	360(120)	850(150)	220(120)	180(120	-50(100)

[a] anisotropic temperature factor; [b] no meaningful temperature factor.

[c] All subsequent atoms were refined as parts of rigid phenyl rings, and no atomic e.s.d.'s are available.

TABLE 4.5

Interatomic distances and angles for $Ru(PhCOS)_2(PMe_2Ph)$(etdiphos)

Estimated standard deviations are given in brackets.

Interatomic distances (Å)

Ru-P1	2.27(2)
Ru-P2	2.39(2)
Ru-P3	2.34(2)
Ru-S1	2.46(2)
Ru-O1	2.09(4)
Ru-S2	2.35(2)
P1-C2	1.94(7)
P1-C3	1.82(4)
P1-C9	1.79(4)
P2-C1	1.85(6)
P2-C15	1.85(4)
P2-C21	1.80(3)
C1-C2	1.43(10)
P3-C27	2.02(8)
P3-C28	1.90(7)
P3-C29	1.82(2)
S1-O1	2.54(4)
S1-C35	1.92(5)
C35-O1	1.44(7)
C35-C36	1.32(6)
S2-C42	1.66(8)
C42-O2	1.11(13)
C42-C43	1.56(9)
O3-C49	1.70(15)
O3-O2	3.0(2)

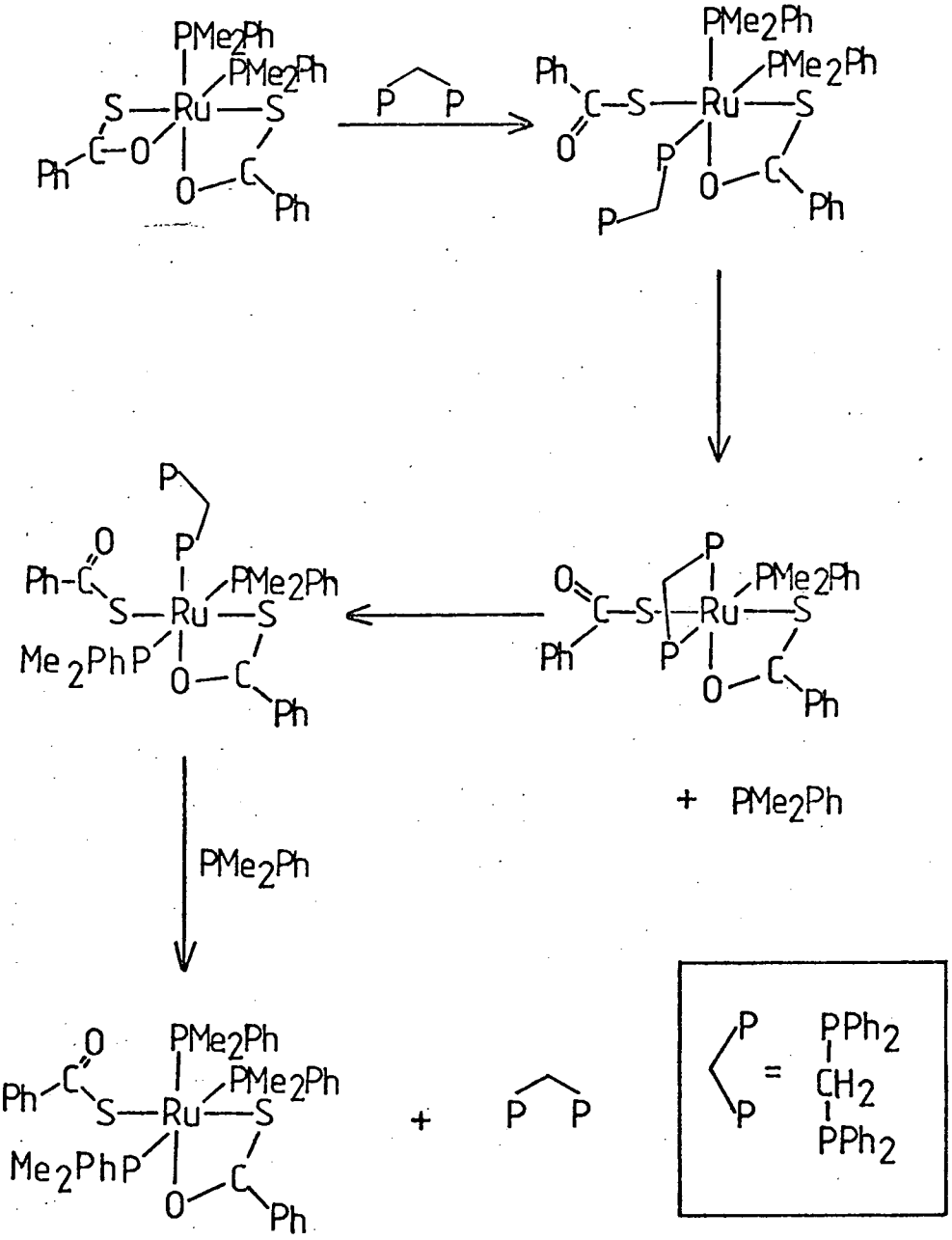
Interatomic Angles (°)

P1-Ru-P2	84.6(6)
P1-Ru-P3	98.8(7)
P1-Ru-S1	161.4(8)
P1-Ru-S2	89.0(8)
P1-Ru-O1	96.1(12)
P2-Ru-P3	174.7(8)

Interatomic angles (°) (Contd.)

P2-Ru-S1	86.6(7)
P2-Ru-S2	88.7(7)
P2-Ru-S1	91.2(7)
P3-Ru-S2	87.2(7)
P3-Ru-O1	95.4(11)
S1-Ru-O2	107.2(7)
S1-Ru-O1	67.2(12)
S2-Ru-O1	173.8(10)
Ru-P1-C2	104(2)
Ru-P1-C3	115(2)
Ru-P1-C9	124(1)
C2-P1-C3	100(2)
C2-P1-C9	108(3)
C3-P1-C9	103(1)
Ru-P2-C1	110(2)
Ru-P2-C15	116(1)
Ru-P2-C21	112(1)
C1-P2-C15	98(2)
C1-P2-C21	113(2)
C15-P2-C21	108(1)
P2-C1-C2	106(4)
P1-C2-C1	115(6)
Ru-P3-C27	117(2)
Ru-P3-C28	118(2)
Ru-P3-C29	114(1)
C27-P3-C28	100(3)
C27-P3-C29	108(2)
C28-P3-C29	97(2)
Ru-S1-C35	84(2)
Ru-O1-C35	112(3)
S1-C35-O1	97(3)
S1-C35-C36	131(3)
O1-C35-C36	131(3)
Ru-S2-C42	114(4)
S2-C4-O2	125(7)
S2-C42-C43	115(6)
O2-C42-C43	119(6)

SCHEME 4.1



Proposed mechanism of reaction of $Ru(PhCOS)_2(PMe_2Ph)_2$ with $Ph_2PCH_2PPh_2$

CHAPTER 5

REACTION OF $RuCl_2(PR_3)_{3 \text{ or } 4}$ COMPOUNDS WITH MONOTHIOBENZOATE ION

5(i) Introduction

The reactions of $RuCl_2(PR_3)_{3 \text{ or } 4}$ compounds (PR_3 = tertiary phosphine, phosphinite, phosphonite or phosphite) with a wide range of dithioacid ligands have recently been studied[101] under varying conditions. In all cases, the product obtained in ethanol under prolonged reflux was $Ru(S\text{-}S)_2(PR_3)_2$. However, the reactions of cis-$RuCl_2(PMe_2Ph)_4$ and $RuCl_2(P(OR)Ph_2)_3$ (R = Me or Et) were particularly sensitive to reaction conditions and a series of intermediates which preceded the formation of $Ru(S\text{-}S)_2(PR_3)_2$ could be isolated. For example, shaking these compounds at room temperature in benzene with $NaS_2PR'_2$ gave the complexes $RuCl(S_2PR'_2)(PR_3)_3$ which readily rearranged in alcoholic solution to give the five-coordinate cations $[Ru(S_2PR'_2)(PR_3)_3]^+$. In contrast, shaking with NaS_2COMe gave $Ru(S_2COMe)_2(PR_3)_3$ (six-coordinate with both unidentate and bidentate xanthate groups) and, in the case of $RuCl_2(PMe_2Ph)_4$, short reaction times in ethanol or benzene with $NaS_2CNR'_2$ gave $[Ru(S_2CNR'_2)(PMe_2Ph)_4]^+$ and $Ru(S_2CNR'_2)_2(PMe_2Ph)_3$ respectively. On the basis of these reactions, a general mechanism has been proposed (Scheme 5.1) for the formation of $Ru(S\text{-}S)_2(PR_3)_2$ complexes from $RuCl_2(PR_3)_{3 \text{ or } 4}$. The work described in this chapter was undertaken to establish whether an analogous mechanism, leading to similar products, operates in the reaction of $RuCl_2(PR_3)_{3 \text{ or } 4}$ with monothiobenzoate ion.

5(ii) Results and Discussion

(a) When $RuCl_2(PMe_2Ph)_4$ was refluxed in ethanol with an excess of ammonium monothiobenzoate, an orange product analysing for $Ru(PhCOS)_2(PMe_2Ph)_3$ was isolated in high yield. The complex gave a non-conducting solution in CH_2Cl_2 and in the i.r. spectrum (see Table 5.1) $\nu_{(CS)}$ at 930, 960 cm^{-1} and $\nu_{(CO)}$ at 1540, 1575 cm^{-1} suggest that both S-bonded unidentate and bidentate monothiobenzoate groups are present.

The ^1H-n.m.r. spectra of the compound (see Table 5.2) show a 1:2:1 "virtually coupled" triplet at 1.57δ in the room-temperature spectrum and, at lower temperature (250K) an additional doublet appears at 1.22δ (J(PH) = 8.5 Hz). These patterns decouple at frequencies equivalent to ^{31}P chemical shifts of ca 6 p.p.m. (triplet) and ca 21 p.p.m. (doublet), and the room-temperature $^{31}P-\{^1H\}$-n.m.r. spectrum, which is poorly resolved, shows resonances at 4.22 p.p.m., 13.10 p.p.m. and 26.80 p.p.m. At lower temperature (220K) the $^{31}P-\{^1H\}$-n.m.r. spectrum exhibits three well-resolved AX_2 patterns with the triplets occurring between 18 and 29 p.p.m. and doublets between 3 and 6 p.p.m., in agreement with the decoupling frequencies determined from the ^1H-n.m.r. studies. Hence, the complex must contain a meridional arrangement of phosphines, with the "virtually coupled" triplet in the ^1H-n.m.r. spectrum arising from the methyl groups on the trans phosphines. The relative intensities of the AX_2 patterns in the $^{31}P-\{^1H\}$-n.m.r. spectrum are approximately 1:3:4 in a freshly made solution and two isomers of mer-$Ru(PhCOS)_2(PMe_2Ph)_3$ can be proposed as the two principal species in the solution (34a and b)*. An isomer such

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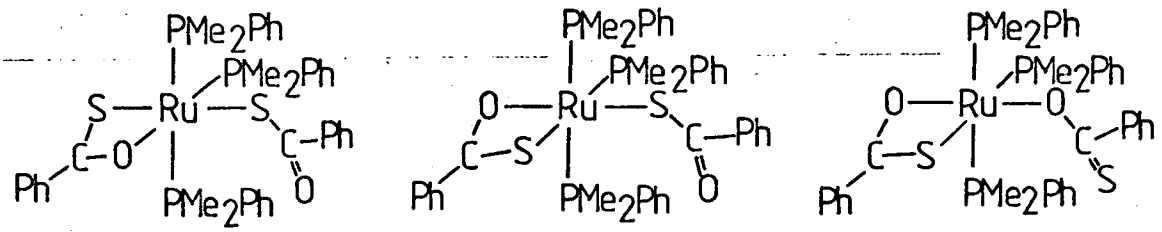
*The coordination of the unidentate monothiobenzoate groups found in the X-ray structure determinations described in Chapters 2,3 and 4, and the i.r. evidence for mer-$Ru(PhCOS)_2(PMe_2Ph)_3$ itself all suggest that unidentate coordination through sulphur is preferred in Ru(II) monothiobenzoate complexes.



(a) (b) (c)

(34)

as (34c) is proposed as the minor species which is present only in small amounts. In each case, the unique phosphine gives rise to the triplet in the $^{31}P-\{^{1}H\}$-n.m.r. AX_2 pattern, and the position of the triplet will be sensitive to the nature of the trans atom. The three triplets appear at 20.55 p.p.m. and 28.64 p.p.m. for the principal isomers and at 18.05 p.p.m. for the minor species. Since in the case of $Ru(PhCOS)_2(PMe_2Ph)_2$ the phosphines trans to oxygen have a chemical shift of 39.00 p.p.m. (see Chapter 2), it seems reasonable to assign the triplet at 28.64 p.p.m. to a phosphine trans to oxygen in the present case, and thus the three AX_2 patterns can be assigned as follows:

	(34a)	(34b)	(34c)
triplet	28.64 p.p.m.	20.55 p.p.m.	18.05 p.p.m.
doublet	5.34 p.p.m.	3.38 p.p.m.	5.05 p.p.m.
J(PP)	33.0 Hz	30.0 Hz	30.0 Hz

On this basis it seems likely that the unique phosphine in the minor isomer is trans to sulphur, as shown (34c). The $^{31}P-\{^{1}H\}$-n.m.r. spectrum obtained from the same solution after it had been stored for three days consists of the single AX_2 pattern assigned above to isomer (34b), which is presumably the thermodynamically favoured species*.

When $RuCl_2(PMe_2Ph)_4$ was shaken in benzene at room temperature with

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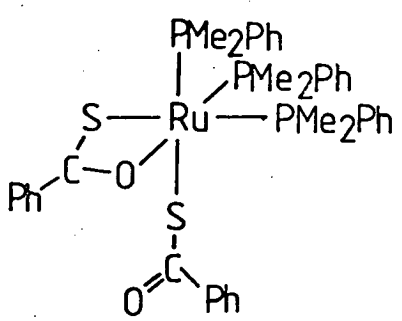
*The same compound, with the same spectroscopic properties, was obtained by reacting $Ru(PhCOS)_2(PMe_2Ph)_2$ with excess PMe_2Ph in ethanol under reflux.

excess ammonium monothiobenzoate, a bright yellow product also analysing for $Ru(PhCOS)_2(PMe_2Ph)_3$ was obtained in high yield. It gave a non-conducting solution in $CH_2C\ell_2$, and again the i.r. spectrum indicates the presence of both S-bonded unidentate and bidentate monothiobenzoate groups.

The ^1H-n.m.r. spectrum at low temperature (240K), however, shows three doublets at 1.14δ, 1.38δ and 1.94δ, which decouple at frequencies equivalent to ^{31}P chemical shifts of ca 16 p.p.m. for the doublets below 1.5δ and ca 27 p.p.m. for the doublet at 1.94δ. The $^{31}P-\{^1H\}$-n.m.r. spectrum is poorly resolved at room temperature, but at low temperature (240K), a second-order ABX pattern is observed (see Figure 5.1) and refinement using the computer programme LAOCOON[124] gave final values for chemical shifts and coupling constants of:

shifts	A	11.73 p.p.m.	J(PP)	AB	26.2 Hz
	B	15.76 p.p.m.		AX	32.3 Hz
	X	28.16 p.p.m.		BX	30.4 Hz

All the coupling constants are of a size typical of couplings between cis phosphines[108] attached to ruthenium(II), and a facial arrangement of phosphines is proposed (35).



(35)

Here, one phosphine is trans to oxygen and can be confidently assigned the ^{31}P chemical shift of 28.16 p.p.m., while the two phosphines trans to sulphur are assigned the two remaining values, which are only ca

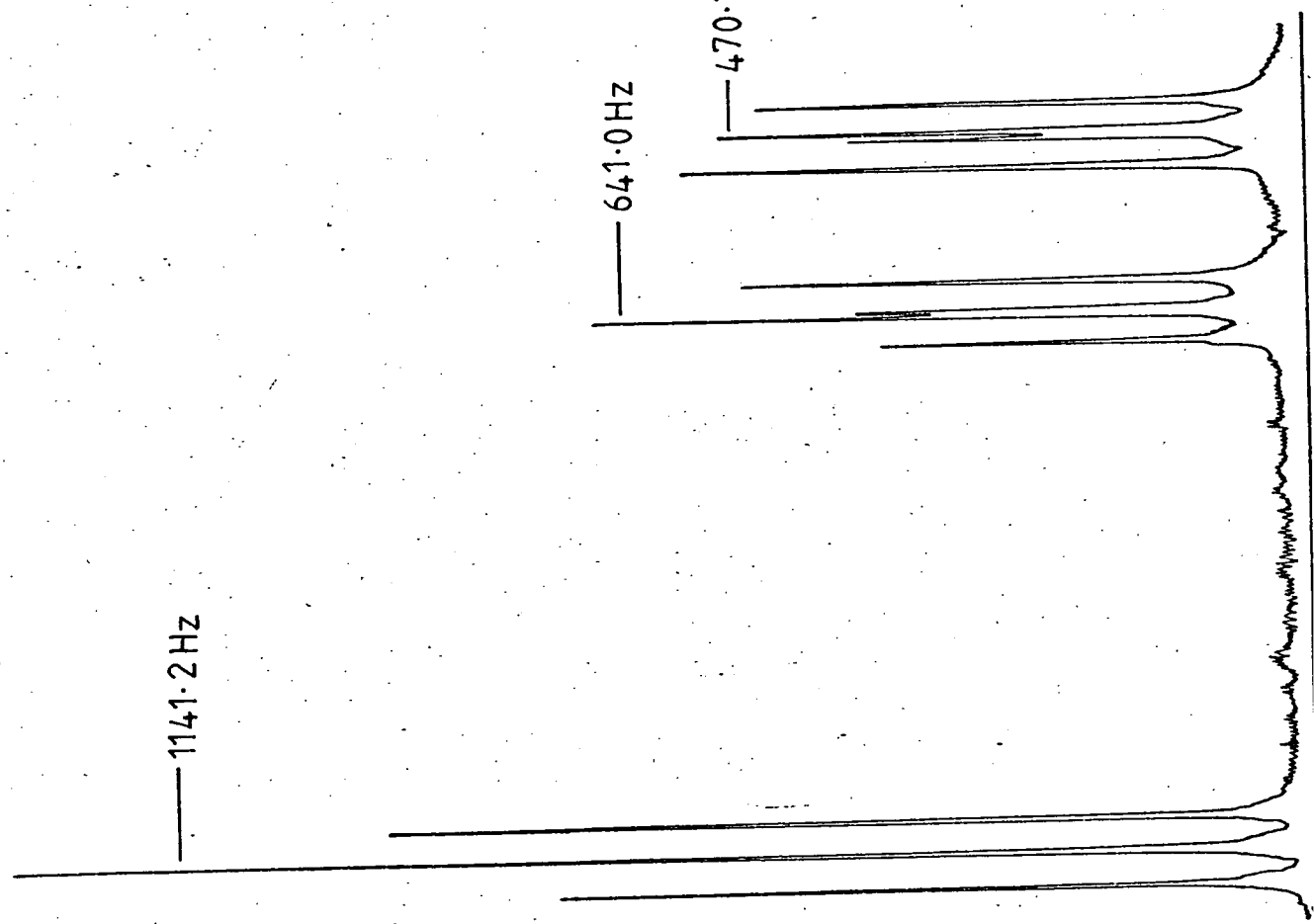


FIGURE 5.1 Observed $^{31}P-[^{1}H]$-n.m.r. spectrum of <u>fac</u>-$Ru(PhCOS)_2(PMe_2Ph)_3$

ABX spin system

shifts:	11·73 ppm	A
	15·76 ppm	B
	28·16 ppm	X
J_{AB}	: 26·2 Hz	
J_{AX}	: 32·3 Hz	
J_{BX}	: 30·4 Hz	

FIGURE 5.1 Computer simulated $^{31}P-\{^1H\}$-n.m.r. spectrum of fac-$Ru(PhCOS)_2(PMe_2Ph)_3$

160 Hz apart and could not be distinguished in the decoupling experiments on the ^{1}H-n.m.r. spectrum.

The same isomer, fac-$Ru(PhCOS)_2(PMe_2Ph)_3$, was obtained by shaking $RuCl_2(PMe_2Ph)_4$ with excess ammonium monothiobenzoate in methanol at room temperature for a few minutes, and fac-$Ru(PhCOS)_2(PMe_2Ph)_3$ converted to the meridional isomer discussed above when it was refluxed in ethanol. Thus, it seems that the facial isomer is formed first in either polar or non-polar solvents, then rearranges on refluxing to give the meridional isomer, which is presumably more thermodynamically stable.

When $RuCl_2(PMe_2Ph)_4$ was shaken in methanol with ammonium monothiobenzoate and the solution was allowed to stand undisturbed for a few hours, a product was isolated on addition of sodium tetraphenylborate which analysed for $[Ru(PhCOS)(PMe_2Ph)_4][BPh_4]$. The compound gave a highly conducting solution in CH_2Cl_2 and the i.r. spectrum indicates only bidentate coordination of the monothiobenzoate ligand ($\nu_{(CS)}$ at 956 cm^{-1}, $\nu_{(CO)}$ at 1490 cm^{-1}).

In the room-temperature ^{1}H-n.m.r. spectrum a "virtually coupled" 1:2:1 triplet is observed at 1.21δ, and two doublets at 1.60δ and 1.86δ; these patterns decouple at frequencies equivalent to ^{31}P chemical shifts of ca 1 p.p.m., ca 19 p.p.m. and ca 9 p.p.m. respectively. In the ^{31}P-$\{^{1}H\}$-n.m.r. spectrum, a second-order A_2BC pattern is observed (see Figure 5.2), and refinement using the computer program NUMARIT[125] of chemical shifts and coupling constants estimated from the observed spectrum gave final values of:

shifts	A	0.59 p.p.m.	J(PP)	AB	26.8 Hz
	B	8.33 p.p.m.		AC	31.2 Hz
	C	19.72 p.p.m.		BC	28.9 Hz

Clearly, the cation has the structure (36)

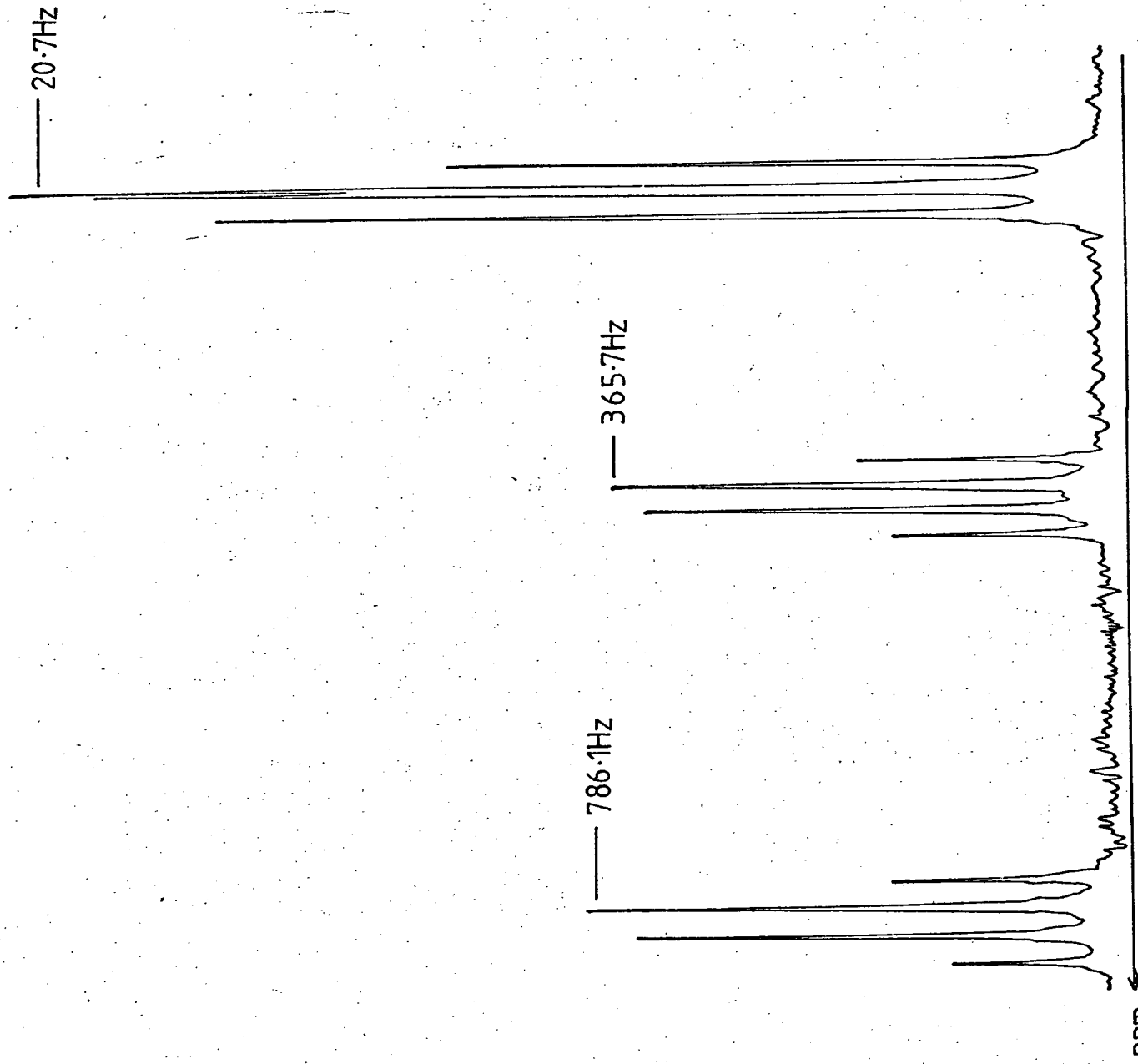
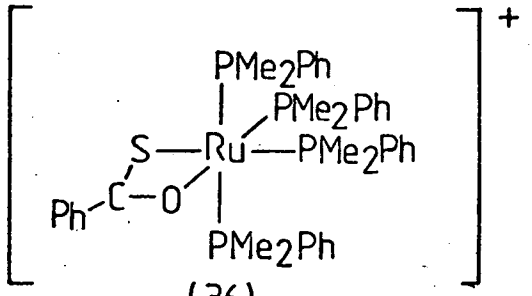


FIGURE 5.2 Observed $^{31}P-[^{1}H]$-n.m.r. spectrum of $[Ru(PhCOS)(PMe_2Ph)_4][BPh_4]$

FIGURE 5.2 Computer simulation of the $^{31}P-\{^{1}H\}$-n.m.r. spectrum of $[Ru(PhCOS)(PMe_2Ph)_4][BPh_4]$



(36)

and the trans phosphines give rise to the ^{31}P resonance at 0.59 p.p.m., associated with the "virtually coupled" triplet in the ^{1}H-n.m.r. spectrum. The B and C resonances, and their associated doublets in the ^{1}H-n.m.r. spectrum, arise from the two cis phosphines and it seems reasonable to assign the resonance at 19.72 p.p.m. to the phosphine trans to oxygen, and that at 8.33 p.p.m. to the phosphine trans to sulphur. Presumably the cation is initially formed by reaction of $RuCl_2(PMe_2Ph)_4$ with one molecule of NH_4PhCOS, and a second monothiobenzoate group then displaces one of the trans phosphines to give fac-$Ru(PhCOS)_2(PMe_2Ph)_3$. This suggestion is supported by the fact that the tetrakis-phosphine cation can only be isolated in the presence of excess PMe_2Ph*, which presumably inhibits the loss of a coordinated phosphine. The cation was also obtained by treating fac-$Ru(PhCOS)_2(PMe_2Ph)_3$ with PMe_2Ph in methanol.

The reactions of $RuCl_2(PMe_2Ph)_4$ with ammonium monothiobenzoate are summarised in Scheme 5.2. Apparently the carbonyl oxygen of the unidentate monothiobenzoate group lacks the ability to displace one of the strongly coordinated PMe_2Ph groups to give the expected fully chelated complex $Ru(PhCOS)_2(PMe_2Ph)_2$.

(b) When $RuCl_2(PMePh_2)_4$ was reacted with excess ammonium monothiobenzoate in ethanol under reflux, or in benzene at room temperature, a product analysing for $Ru(PhCOS)_2(PMePh_2)_3$ was isolated. The compound gave a

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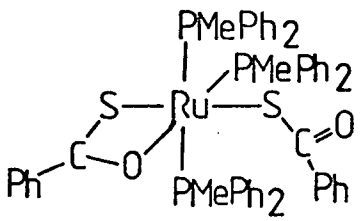
* All the reaction mixtures containing $RuCl_2(PMe_2Ph)_4$ or $RuCl_2(PMePh_2)_4$ smelt strongly of free tertiary phosphine after a few minutes.

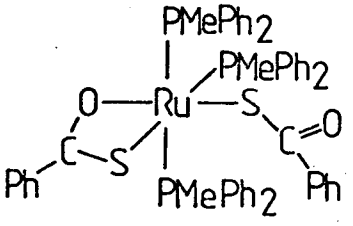
non-conducting solution in $CH_2C\ell_2$ and the i.r. spectrum indicates the presence of both S-bonded unidentate and bidentate monothiobenzoate groups.

The methyl region of the room-temperature ^1H-n.m.r. spectrum consists of a "pseudo-triplet" pattern at 1.59δ (see definition in Chapter 2, p. 38), a "virtually coupled" 1:2:1 triplet at 1.93δ and two doublets at 1.71δ and 1.89δ. These patterns decouple when irradiated at frequencies equivalent to ^{31}P chemical shifts of ca 46 p.p.m., ca 14 p.p.m., ca 33 p.p.m. and ca 30 p.p.m. respectively, and the ^{31}P-{^1H}-n.m.r. spectrum at room temperature contains singlets at 45.58 p.p.m. and 35.90 p.p.m. together with three AX_2 patterns with triplets at 20-33 p.p.m. and doublets between 13 and 16 p.p.m. Clearly the 1:2:1 triplet in the ^1H-n.m.r. spectrum is associated with the doublets in the ^{31}P spectrum, and the doublets in the ^1H spectrum with the two strongest ^{31}P triplets. The ^1H "pseudo-triplet" is associated with the strong singlet in the ^{31}P spectrum, and hence the species present in the solution at room temperature can be identified as three species containing three phosphines in a meridional arrangement and one isomer of $Ru(PhCOS)_2(PMePh_2)_2$ containing equivalent cis-phosphines. The singlet at 35.90 p.p.m. may arise from a second isomer of $Ru(PhCOS)_2(PMePh_2)_2$ containing equivalent phosphines, but in view of the analytical results, which do not agree with a formula including an appreciable amount of $Ru(PhCOS)_2(PMePh_2)_2$, it seems more likely that this singlet arises from methyldiphenylphosphine oxide, formed from free $PMePh_2$ which is released from the tris-phosphine complex to give the isomer of $Ru(PhCOS)_2(PmePh_2)_2$ already identified in solution. At lower temperatures (240K) a fourth small AX_2 pattern appears in the ^{31}P-{^1H}-n.m.r. spectrum, with a triplet at 19.50 p.p.m. and a doublet at 13.18 p.p.m., indicating that four species are present containing a meridional arrangement of three phosphines.

The two possible isomers of mer-$Ru(PhCOS)_2(PMePh_2)_3$ containing an S-bonded unidentate monothiobenzoate group (see i.r. evidence) can be assigned to the two strongest AX_2 patterns (37a and b), and by analogy



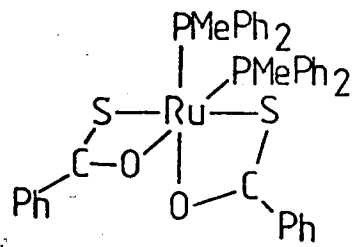
(a)



(b)

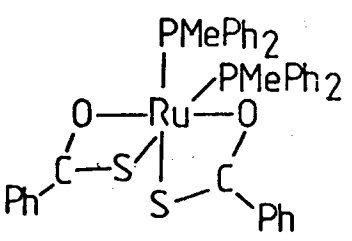
(37)

with the spectra of mer-$Ru(PhCOS)_2(PMe_2Ph)_3$ it seems reasonable to assign the isomer (37a), containing a phosphine trans to oxygen, to the pattern with its triplet at 32.92 p.p.m. (300K) and J(PP), 32.5 Hz, and the isomer (37b) to the pattern with its triplet at 29.52 p.p.m. and J(PP), 30.3 Hz. Thus, the resonance of the phosphine trans to oxygen is at a higher frequency than that trans to sulphur, and the sizes of the two coupling constants also compare well with those found in the corresponding mer-$Ru(PhCOS)_2(PMe_2Ph)_3$ species (33.0 Hz for PMe_2Ph trans to oxygen, 30.0 Hz for PMe_2Ph trans to sulphur). The ^{31}P singlet at 45.58 p.p.m. and the associated ^1H "pseudo-triplet" pattern arise from an isomer of $Ru(PhCOS)_2(PMePh_2)_2$ containing equivalent cis-phosphines (38a or b) and



(a)

(38)



(b)

the high frequency of the ^{31}P resonance suggests that the phosphines are probably trans to oxygen (38a).

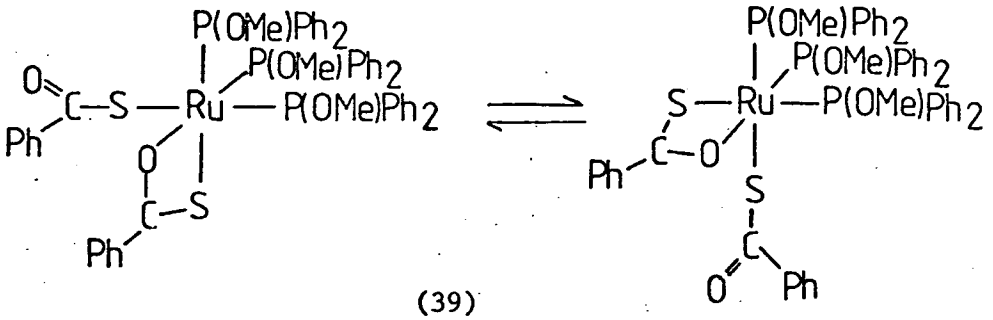
The presence of $Ru(PhCOS)_2(PMePh_2)_2$ in the solution, as well as $Ru(PhCOS)_2(PMePh_2)_3$, shows that the uncoordinated monothiobenzoate oxygen does have a limited ability to displace a molecule of $PMePh_2$, which is both a weaker Lewis base than PMe_2Ph, and more subject to steric crowding when three phosphines are coordinated to a single metal. There is no sign of the formation of a facial isomer, even in benzene, or of a tetrakis-phosphine cation, and this may also be a reflection of the steric hindrance associated with a phosphine bearing two phenyl rings. Even in dithioacid systems, the cations are observed only in the case of PMe_2Ph. There is no significant change in the relative amounts of the different complexes in solution after standing for several days, except for a slight increase in the amount of $Ru(PhCOS)_2(PMePh_2)_2$. As in the case of mer-$Ru(PhCOS)_2(PMe_2Ph)_3$, the minor isomers in solution probably contain O-bonded unidentate monothiobenzoate groups, but as expected from previous observations, the i.r. evidence indicates that unidentate S-bonding predominates.

(c) When $RuCl_2(P(OMe)_2Ph)_4$ was reacted with excess ammonium monothiobenzoate in ethanol under reflux, a deep red solution resulted, but the dark brown product obtained on cooling and partial evaporation of the solvent showed no bands in the i.r. spectrum characteristic of the monothiobenzoate ligand and no identifiable ^1H-n.m.r. or $^{31}P-\{^1H\}$-n.m.r. resonances. A problem that has been encountered before when $P(OMe)_2Ph$ and $P(OMe)Ph_2$ complexes are reacted in ethanol solvent[99] is trans-esterification of the free phosphonite or phosphinite released in the reaction to give $P(OEt)_2Ph$ and $P(OEt)Ph_2$ which can exchange with coordinated ligands; hydrolysis of the P-OMe function to give P-OH and $P-O^-$ is also possible, and the overall result is to give mixed, impure products.

However, reaction of $RuCl_2(P(OMe)_2Ph)_4$ with excess ammonium monothiobenzoate in benzene at room temperature yielded a yellow compound. In the i.r. spectrum, $\nu_{(CS)}$ at 970 cm^{-1} and $\nu_{(CO)}$ at 1555 cm^{-1} are not inconsistent with the presence of both S-bonded unidentate and bidentate monothiobenzoate groups, since both the $\nu_{(CO)}$ and $\nu_{(CS)}$ regions of the spectrum were largely masked by other ligand vibrations. In the room-temperature ^1H-n.m.r. spectrum a group of resonances is observed between 3.50 and 3.70δ, and a doublet at 3.79δ which decouples at a frequency equivalent to ^{31}P chemical shift of ca 35 p.p.m. No other decoupling frequency could be found and since coordinated $P(OMe)_2Ph$ groups have ^{31}P chemical shifts greater than 150 p.p.m., the ^1H-n.m.r. study was abandoned. In the $^{31}P-\{^1H\}$-n.m.r. spectrum strong resonances are observed between 24 and 28 p.p.m., and these are ascribed to P(V) species produced by an Arbuzov reaction of $P(OMe_2)_2Ph$ to give tertiary phosphine oxide species[126]. The room temperature spectrum also contains resonances above 150 p.p.m., and on cooling to 250K this section of the spectrum can be interpreted as a strong singlet at 150.64 p.p.m. and an AB_2 pattern. Refinement using the computer program LAOCOON[124] of chemical shifts and a coupling constant estimated from the observed spectrum gave final values for the AB_2 parameters of:

shifts	A	152.95 p.p.m.	J(PP)	43.61 Hz
	B	162.66 p.p.m.		

Thus, the section of the spectrum above 150 p.p.m. can be ascribed to two species in solution, viz. an isomer of $Ru(PhCOS)_2(P(OMe)_2Ph)_2$ containing magnetically equivalent phosphonite groups and an isomer of $Ru(PhCOS)_2(P(OMe)_2Ph)_3$ which contains either a meridional arrangement of phosphonites or a facial arrangement (39) in which rapid interconversion of the two optical isomers would make the A phosphorus atoms equivalent.



(39)

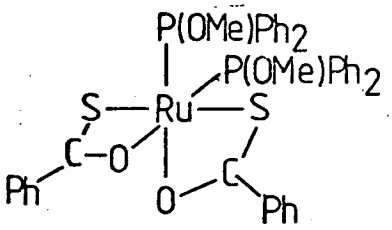
Since the spectrum was recorded at a temperature (250K) at which some slowing down of this isomerisation would be expected, making the A phosphonites inequivalent, the meridional arrangement of phosphonites seems more likely, but a definite conclusion must await a more informative ^{1}H-n.m.r. study.

Once again, the oxygen of the monothiobenzoate group is shown to have a limited ability to displace a coordinated PR_3 group; an appreciable amount of the tris-phosphonite complex is present in the product, while dithioacid ligands have been shown[101] to form $Ru(S\text{-}S)_2(P(OMe)_2Ph)_2$ compounds quite readily.

(d) When $RuCl_2(P(OMe)Ph_2)_3$ was reacted with excess ammonium monothiobenzoate in ethanol under reflux, a red solution was obtained and the red product that was isolated proved impossible to characterise. The same problems of transesterification and hydrolysis of the P-OMe function apply as were discussed above for $RuCl_2(P(OMe)_2Ph)_4$. However, when the reaction was carried out in benzene at room temperature, a yellow product was obtained which analysed for $Ru(PhCOS)_2(P(OMe)Ph_2)_2$ and the i.r. spectrum indicates the presence of bidentate monothiobenzoate groups only.

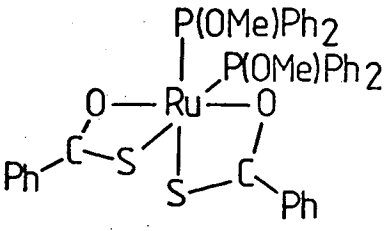
The ^{1}H-n.m.r. spectrum at room temperature exhibits a doublet at 3.26δ which decouples when irradiated at a frequency equivalent to a ^{31}P chemical shift of ca 154 p.p.m. On cooling to 250K the spectrum

exhibits two doublets at 3.24δ and 3.34δ which both decouple at ca 155 p.p.m. The $^{31}P-\{^{1}H\}$-n.m.r. spectrum consists at room temperature of a singlet at 151.08 p.p.m. which shifts to 150.55 p.p.m. on cooling to 240K, but shows no sign of splitting. The solution structure of $Ru(PhCOS)_2(P(OMe)Ph_2)_2$ prepared in benzene must therefore contain a cis arrangement of magnetically equivalent phosphinite groups (40a or b)



(a)

(40)



(b)

and the appearance of the ^{1}H-m.m.r. resonances of the methyl groups as doublets indicates that the coupling between the two phosphorus atoms is small compared to the phosphorus-hydrogen coupling. The inequivalence of the two methyl groups at low temperature must be due to the "freezing out" of two conformers of the complex in which steric interactions with neighbouring groups make the two methyls magnetically inequivalent, while the phosphorus atoms remain equivalent.

5(iii) Conclusions

The products obtained from the reaction of $RuCl_2(PR_3)_{3 \text{ or } 4}$ compounds with ammonium monothiobenzoate depend both on the nature of the PR_3 group used and on the reaction conditions. The tris-phosphine species $Ru(PhCOS)_2(PR_3)_3$, containing one unidentate monothiobenzoate group, is obtained as the only product when $PR_3 = PMe_2Ph$, and as the principal product when $PR_3 = PMePh_2$ or $P(OMe)_2Ph$, because the carbonyl oxygen is apparently unable to displace a PR_3 molecule to form a second chelate

ring. Indeed, in the case of PMe_2Ph, excess phosphine will rupture one of the Ru-O bonds in $Ru(PhCOS)_2(PMe_2Ph)_2$ to give the tris-phosphine species. This underlines the contrast with chelated dithioacid systems of the type $Ru(S-S)_2(PR_3)_2$ where Lewis bases such as carbon monoxide will often displace a phosphine in preference to attacking the Ru-S bonds to give unidentate acid groups[99].

Bearing in mind this inability of the carbonyl oxygen to displace strongly bound phosphine groups, and the nature of the species isolated from the reaction of $RuCl_2(PMe_2Ph)_4$ with ammonium monothiobenzoate under various conditions, the mechanism shown in Scheme 5.3 is proposed for the formation of mer-$Ru(PhCOS)_2(PR_3)_3$ complexes from $RuCl_2(PR_3)_3$ or 4. The mechanism is analogous to that proposed for the formation of $Ru(S-S)_2(PR_3)_2$ complexes[101] (Scheme 5.1) with the exception of the final step in which the unidentate acid displaces a PR_3 group to form a second chelate ring. That step apparently does occur, however, even under mild conditions, where $PR_3 = P(OMe)Ph_2$, which may be more readily displaced for steric reasons. In the analogous reactions with dithioacids, it was found[101] that intermediates in the formation of $Ru(S-S)_2(PR_3)_2$ could be isolated when $PR_3 = PMe_2Ph$ or $P(OMe)Ph_2$, but not when $PMePh_2$ or $P(OMe)_2Ph$ was used. In the reactions with monothiobenzoate ion, however, $Ru(PhCOS)_2(PR_3)_2$ is obtained as the exclusive product only when $PR_3 = P(OMe)Ph_2$, and none of the bis-phosphine product is obtained when PMe_2Ph is used, and this reflects the weaker coordinating power of the carbonyl oxygen as compared with sulphur.

Experimental

Experimental details are as given in the Experimental section of Chapter 2. $RuCl_2(PR_3)_{3 \text{ or } 4}$ compounds were obtained by the method of Armit, Boyd and Stephenson[127], and sodium tetraphenylborate from BDH.

Tris(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II)

Meridional isomers: The compound $RuCl_2(PMe_2Ph)_4$ (0.10g) was refluxed in ethanol (50 ml) with NH_4PhCOS (0.10g) for 2h. The solution was filtered hot to remove NH_4Cl, then the volume was reduced and on cooling the orange product was filtered off (0.08g, 76%) m.p. 176-179°C (Found: C, 57.97; H. 5.55. Calc. for $C_{38}H_{43}O_2P_3RuS_2$: C, 57.80; H, 5.45%). The same complex was also prepared by refluxing $Ru(PhCOS)_2(PMe_2Ph)_2$ (0.10g) in ethanol with PMe_2Ph (0.10g) for 2h, filtering, reducing the volume, and cooling.

Facial isomer: The compound $RuCl_2(PMePh)_4$ (0.10g) was shaken in benzene (20 ml) with NH_4PhCOS (0.10g) at room temperature for 30 min. The solution was filtered and the volume reduced, then after standing 3h, the yellow product was filtered off (0.07g, 68%) m.p. 156-159°C (Found: C, 57.14; H, 5.83. Calc. for $C_{38}H_{43}O_2P_3RuS_2$: C, 57.80; H, 5.45%). The complex was converted to the meridional isomer on refluxing in ethanol for 1h.

Tetrakis(dimethylphenylphosphine)(monothiobenzoato)ruthenium(II) tetraphenylborate

$RuCl_2(PMe_2Ph)_4$ (0.10g) was shaken in methanol (20 ml) with NH_4PhCOS (0.10g) for 30 min. at room temperature, then $NaBPh_4$ (0.05g) was added and the solution allowed to stand for 4h, when the pale yellow product was filtered off (0.08g, 57%) m.p. 160-163°C (Found: C, 68.07;

H, 6.22. Calc. for $BC_{63}H_{69}OP_4RuS$: C, 68.17; H, 6.22%).

Tris(Methyldiphenylphosphine)bis(monothiobenzoato)ruthenium(II)

The compound $RuCl_2(PMePh_2)_4$ (0.10g) was refluxed in ethanol (50 ml) with NH_4PhCOS (0.10g) for 2h. The solution was filtered hot and the volume was reduced; on cooling, the orange product was filtered off (0.08g, 81%) m.p. 98-100°C (Found: C, 65.16; H, 5.07. Calc. for $C_{53}H_{49}O_2P_3RuS_2$: C, 65.23; H, 5.02%). The same complex was obtained when $RuCl_2(PMePh_2)_4$ (0.10g) was shaken in benzene (20 ml) with NH_4PhCOS (0.10g) for 30 min. at room temperature.

Bis(dimethylphenylphosphonite)bis(monothiobenzoato)ruthenium(II) and tris(dimethylphenylphosphonite)bis(monothiobenzoata)ruthenium(II)

The compound $RuCl_2(P(OMe)_2Ph)_4$ (0.10g) was shaken in benzene (20 ml) with NH_4PhCOS (0.10g) for 30 min. at room temperature. The solution was filtered, the volume was reduced, and after standing ca 2h the yellow product was filtered off (0.07g, ca 70%) m.p. 105-110°C (Found: C, 44.97- H, 4.76. Calc. for $C_{38}H_{43}O_8P_3RuS_2$: C, 51.52; H, 4.86. Calc. for $C_{30}H_{32}O_6P_2RuS_2$: C, 50.35; H, 4.48%)

Bis(methyldiphenylphosphinite)bis(monothiobenzoato)ruthenium(II)

The compound $RuCl_2(P(OMe)Ph_2)_3$ (0.10g) was shaken in benzene (20 ml) with NH_4PhCOS (0.10g) for 30 min. at room temperature. The solution was filtered, the volume was reduced, and after standing ca 4h, the yellow product was filtered off (0.07g, 66%) m.p. 111-113°C (Found: C, 59.93; H, 4.91. Calc. for $C_{40}H_{36}O_4P_2RuS_2$: C, 59.48; H, 4.46%).

TABLE 5.1

Mull i.r. spectra of some monothiobenzoate complexes of ruthenium(II) with PR_3 groups.

Compound	PhCOS vibrations (cm^{-1})	
	$\nu_{(CO)}$	$\nu_{(CS)}$
mer-$Ru(PhCOS)_2(PMe_2Ph)_3$	930	1540
	960	1575
fac-$Ru(PhCOS)_2(PMe_2Ph)_3$	932	1550
	965	1585
$[Ru(PhCOS)(PMe_2Ph)_4][BPh_4]$	956	1490
$Ru(PhCOS)_2(PMePh_2)_3$	925	1480
	960	1550
$Ru(PhCOS)_2(P(OMe)_2Ph)_3$	970	1555
$Ru(PhCOS)_2(P(OMe)Ph_2)_2$	965	1570

TABLE 5.2

^{1}H-n.m.r. data in $CDCl_3$ for some monothiobenzoate complexes of ruthenium(II) with PR_3 groups

Compound	T/K	δ ± 0.01 p.p.m. methyl of phosphine	other
mer-$Ru(PhCOS)_2(PMe_2Ph)_3$	300	1.57(t)	7.00 - 8.00[a]
	250	1.22(d)	7.00 - 8.00[a]
		1.57(t)	
fac-$Ru(PhCOS)_2(PMe_2Ph)_3$	300	1.55(u)	7.00 - 8.00[a]
		1.85(d)	
	240	1.14(d)	7.00 - 8.00[a]
		1.38(d)	
		1.94(d)	
$[Ru(PhCOS)(PMe_2Ph)_4][BPh_4]$	300	1.21(t)	7.00 - 8.00[a]
		1.60(d)	
		1.86(d)	
$Ru(PhCOS)_2(PMePh_2)_3$	300	1.59(pt)	7.00 - 8.00[a]
		1.71(d)	
		1.93(t)	
		1.89(d)	
$Ru(PhCOS)_2(P(OMe)Ph_2)_2$	300	3.26(d)	7.00 - 8.00[a]
	250	3.24(d)	7.00 - 8.00[a]
		3.34(d)	

d = doublet pt = pseudo-triplet t = triplet

u = unresolved.

[a] phenyl resonances

TABLE 5.3

$^{31}P-\{^{1}H\}$-n.m.r. data in $CDCl_3$ for some monothiobenzoate complexes of ruthenium(II) with PR_3 groups

Compound	T/K		δ ± 0.01 p.p.m.		$J_{(PP)}$/Hz
mer-$Ru(PhCOS)_2(PMe_2Ph)_3$ (fresh sample)	300		4.22(u)		
			13.10(u)		
			26.83(u)		
	220		3.78(d)		30.0
			5.05(d)		30.0
			5.34(d)		33.0
			18.05(t)		30.0
			20.55(t)		30.0
			28.64(t)		33.0
(after 5 days)	220		3.78(d)		30.0
			20.55(t)		30.0
fac-$Ru(PhCOS)_2(PMe_2Ph)_3$		ABX[a] pattern	A 11.73	AB	26.2
			B 15.76	AX	32.3
			X 28.16	BX	30.4
$[Ru(PhCOS)(PMe_2Ph)_4][BPh_4]$	300	A_2BC[b] pattern	A 0.59	AB	26.8
			B 8.33	AC	31.2
			C 19.72		
$Ru(PhCOS)_2(PMePh_2)_3$	300		13.85(d)		27.7
			13.98(d)		32.5
			15.04(d)		30.3
			20.44(t)		27.5
			29.52(t)		30.3
			32.92(t)		32.5
			35.90(s)		
			45.58(s)		
	240		13.18(d)		26.5
			14.00(d)		27.5
			14.18(d)		32.0
			15.13(d)		30.0
			19.50(t)		26.5
			22.90(t)		27.5
			29.20(t)		30.0
			31.70(t)		32.0
			36.51(s)		
			45.53(s)		

TABLE 5.3 (Contd.)

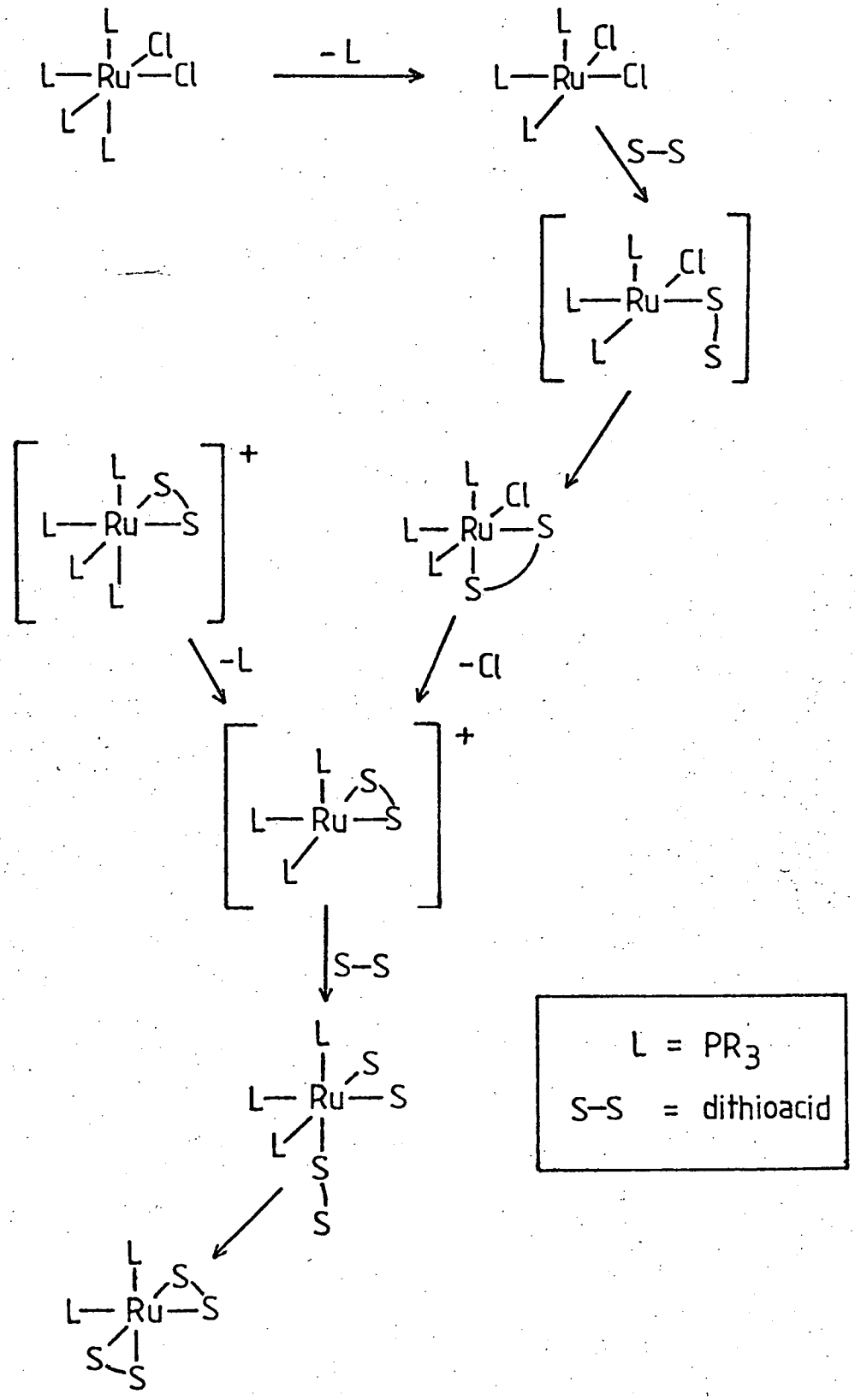
Compound	T/K		δ ± 0.01 p.p.m.	$J_{(PP)}$
$Ru(PhCOS)_2(P(OMe)_2Ph)_3$	300		24.81(u)	
			27.33(u)	
			151.07(s)	
			151.86(d)	2.7
			152.94(d)	2.0
			161. 0(s)	
			162.57(d)	5.0
	250		22.55(s)	
			28.29(s)	
			150.64(s)	
		A_2B[a] pattern A	152.95	AB 43.61
		B	162.66	
$Ru(PhCOS)_2(P(OMe)Ph_2)_2$	300		151.08(s)	
	240		150.55(s)	

d = doublet, s = singlet, t = triplet, u = unresolved

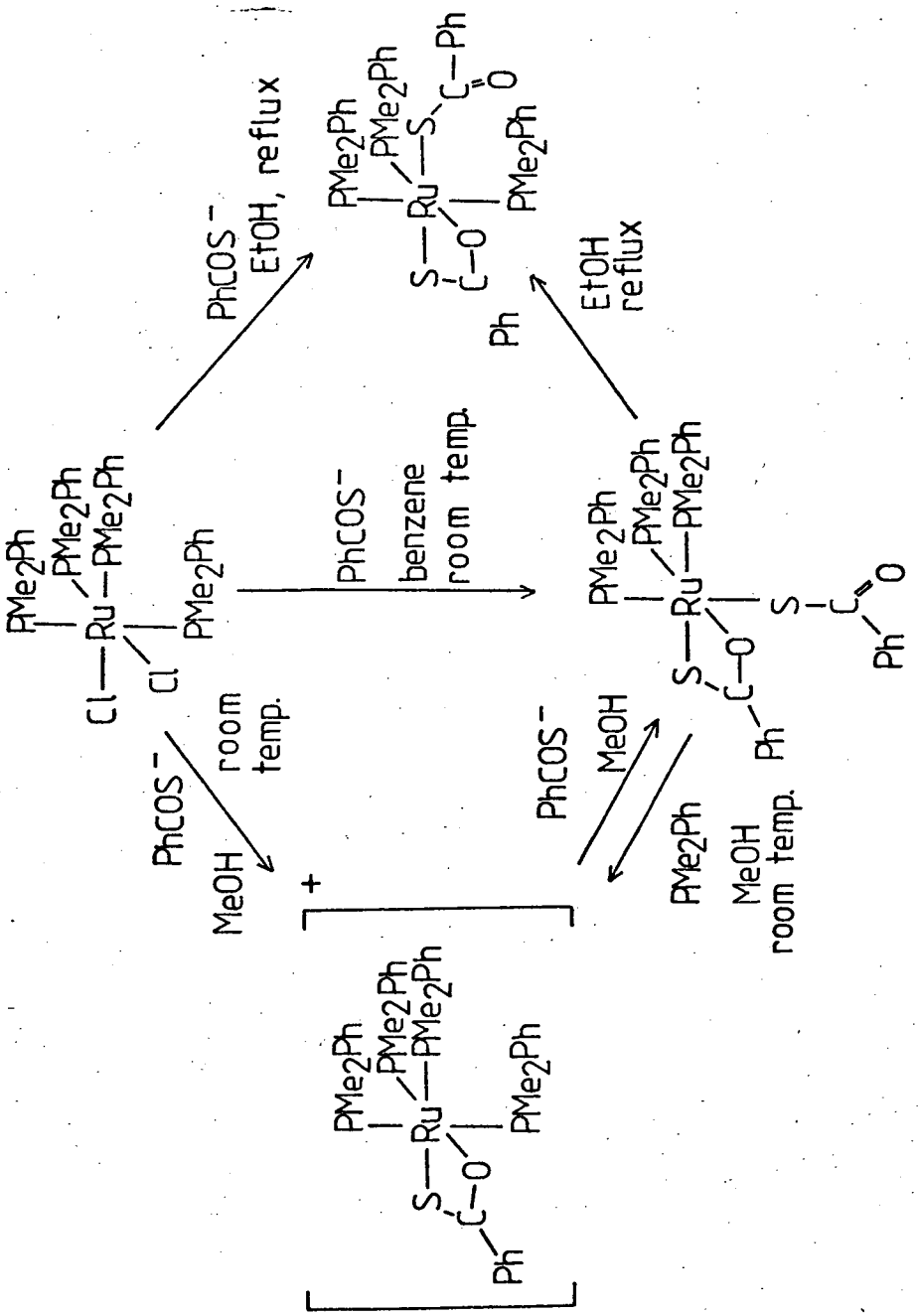
[a]values obtained using computer program LAOCOON[124]

[b]values obtained using computer program NUMARIT[125]

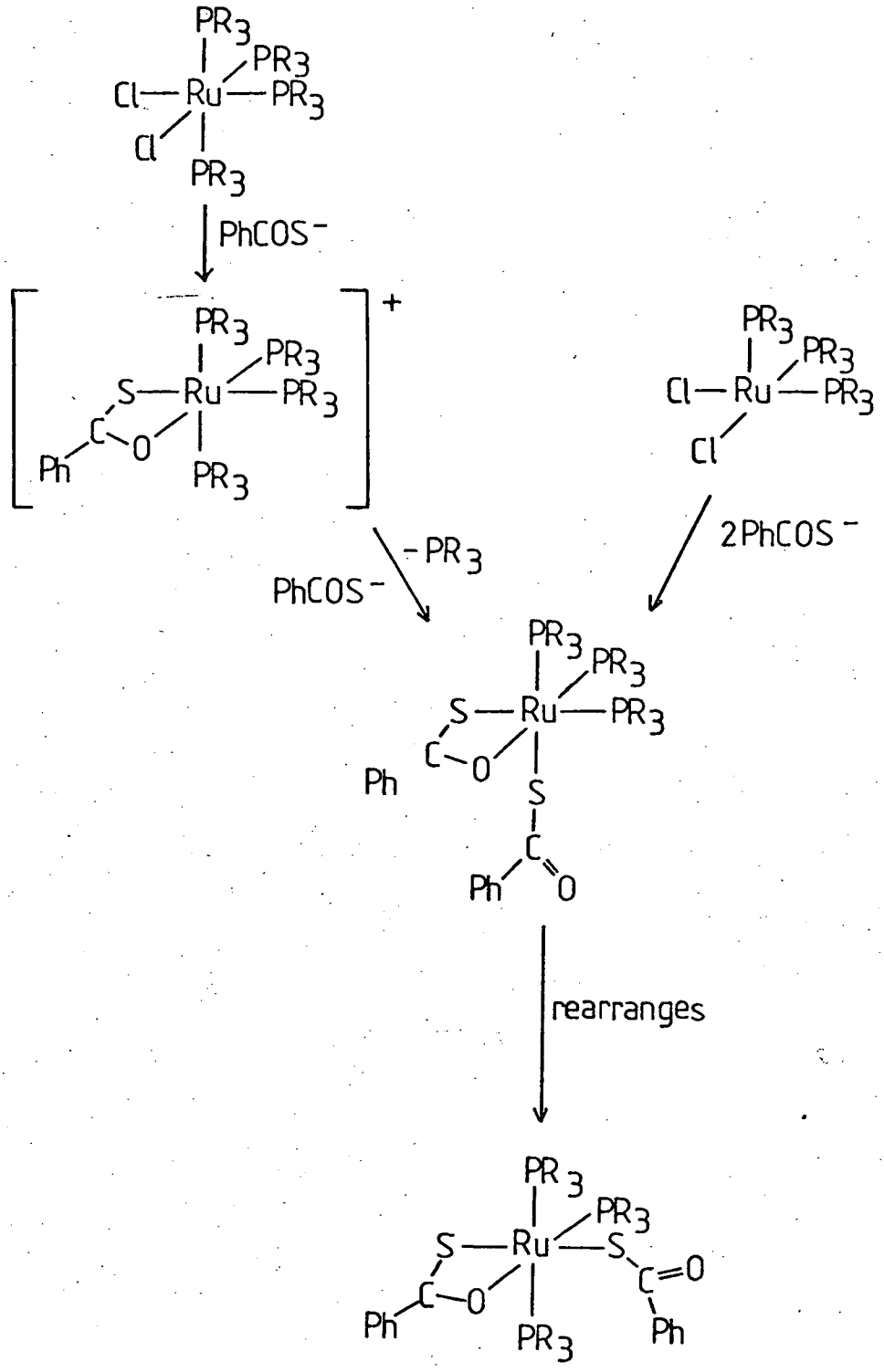
SCHEME 5.1 Proposed mechanism of formation of $Ru(S-S)_2(PR_3)_2$ from $RuCl_2(PR_3)_{3 or 4}$



SCHEME 5.2 Summary of the reactions of $RuCl_2(PMe_2Ph)_4$ with monothiobenzoate ion.



SCHEME 5.3 Proposed mechanism of formation of mer-$Ru(PhCOS)_2(PMe_2Ph)_3$



APPENDIX 1

The Structures of $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$ and $[PhCH_2PPh_3]_2[RuCl_6(CO)].2CH_2Cl_2$

A(i) Introduction

Previous workers[128] have studied the reaction of the doubly chloride-bridged dimer $[RuCl_2(CO)(C_7H_8)]_2$, with excess $PhCH_2PPh_3Cl$ and hydrochloric acid in acetone. After being shaken at room temperature for several days, the reaction mixture yielded an orange crystalline product which was identified on the basis of analytical and spectroscopic data as the anionic Ru(II) complex $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$. Detailed studies of ^1H-n.m.r. and ^{13}C-n.m.r. spectra indicated that the anion contained a facial arrangement of chloride ligands in solution[129].

After removal of this main product, a red solution remained, and upon treatment with light petroleum (b.p. 100/120°C) and dichloromethane a small amount of dark red crystals was recovered. The i.r. spectrum of the compound exhibited a single carbonyl stretching mode at 1994 cm^{-1}, a band at 1270 cm^{-1} indicating the presence of dichloromethane in the crystals, and the characteristic bands associated with the $[PhCH_2PPh_3]^+$ cation, but no band assignable to the diene present in the starting material were observed. The compound gave a conducting solution in dichloromethane and exhibited strong e.s.r. signals suggesting an anionic Ru(III) complex. X-ray structure determinations on both compounds were undertaken to confirm the stereochemistry of the principal product, $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$ and to establish the identity and the stereochemistry of the minor product, which proved to be $[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$.

A(ii) Solution of the Structure of $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$

A crystal of $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$ taken from the reaction mixture was found to be suitable for data collection, and preliminary precession photographs indicated that the crystals were monoclinic with crystal data as follows:

$a = 12.471(5)$ Å

$b = 18.176(2)$ Å

$c = 14.181(4)$ Å

$\beta = 109.84(4)^\circ$

$D_m = 1.50$ g cm^{-3}

$D_c = 1.50$ g cm^{-3}

$z = 4$

$\mu(MoK_\alpha) = 8.5$ cm^{-1}

(The cell dimensions were refined using 25 reflections with θ ca 15°, measured on the diffractometer before data collection.) The photographs also exhibited the systematic absences characteristic of the space group $P2_1/c$ (n°. 14). The crystal was then mounted on an ENRAF-Nonius CAD4 four-circle diffractometer and data were collected out to $\theta = 22^\circ$ using monochromatised MoK_α radiation. Of the reflections measured, some 75% were significant at the 3σ level and 2859 observed reflections were used to solve the structure. After data reduction a Patterson map was calculated, and from this the ruthenium atom was located in the general position (.3860, .1840, .6770). The rest of the non-hydrogen atoms were found without difficulty from a series of three successive Fourier maps and the geometry of the four phenyl rings in the cation was idealised. Least-squares refinement of the atomic parameters was carried out giving anisotropic temperature factors to the Ru, P and Cl atoms and isotropic

temperature factors to the C and O atoms, until a conventional $R = 0.086$ was reached. A further difference Fourier map calculated at that stage revealed that the hydrogen atoms in the cation and in the diene moiety of the anion were visible, and ideal trigonal or tetrahedral positions were calculated for them as appropriate, with a C-H distance of 1.1Å throughout. These hydrogen atom positions were used as a fixed contribution in later cycles and the refinement finally converged with $R = 0.045$. A weighting scheme was applied in the final cycles such that reflections of low $|F_{obs}|$ were given constant weight, and those of higher $|F_{obs}|$ were weighted down (specifically, $W = 1.0$ for $|F_{obs}| \leq 56$, otherwise $W = 56/|F_{obs}|$).

A(iii) Solution of the Structure of $[PhCH_2PPh_3]2[RuCl_5(CO)].2CH_2Cl_2$

Some of the dark red crystals recovered on treatment of the final solution with light petrol and dichloromethane were found to be suitable for X-ray work, and preliminary precession photographs were taken. These revealed that the crystals were orthorhombic with crystal data as follows:

$$a = 13.913(10)\text{Å}$$
$$b = 18.401(9)\text{ Å}$$
$$c = 20.965(9)\text{ Å}$$
$$D_m = 1.40\text{ g cm}^{-3}$$
$$D_c = 1.46\text{ g cm}^{-3}$$
$$z = 4$$
$$\mu(MoK_\alpha) = 8.3\text{ cm}^{-1}$$

(The cell dimensions were refined as described in A(ii)). The preliminary photographs also exhibited the following systematic absences:

In the 0 k ℓ zone, k = 2n + 1 absent

In the h 0 ℓ zone, ℓ = 2n + 1 absent

In the h k 0 zone, h+k = 2n+1 absent.

These absences define the space group uniquely as Pbcn (n^{o}. 60). Data collection was carried out as in A(ii). However, the crystals were not well formed and only some 40% of the recorded reflections were significant at the 3σ level; the structure was solved using 1010 observed reflections. After data reduction, including the application of L_p corrections, a Patterson summation was calculated. The space group Pbcn is centosymmetric and has eight equivalent positions in the unit cell:

$$\pm[x,y,z;\ \tfrac{1}{2}-x,\ \tfrac{1}{2}+y,\ z;\ \ x,\ -y,\ \tfrac{1}{2}+z;\ \ \tfrac{1}{2}+x,\ \tfrac{1}{2}+y,\ \tfrac{1}{2}-z]\ ,$$

giving Patterson peaks on Harker planes at

$$\tfrac{1}{2},\ \tfrac{1}{2}\pm 2y,\ \pm 2z;\ \ \pm 2x,\ 0,\ \tfrac{1}{2}\pm 2z;\ \ \tfrac{1}{2}\pm 2x,\ \tfrac{1}{2}\pm 2y,\ \tfrac{1}{2}$$

and Harker lines at

$$\tfrac{1}{2}\pm 2x,\ \tfrac{1}{2},\ 0;\ \ 0,\ \pm 2y,\ \tfrac{1}{2};\ \ \tfrac{1}{2},\ \tfrac{1}{2},\ \tfrac{1}{2}\pm 2z\ .$$

Points on the Harker lines were identified as follows from the calculated map:

$(2x+\frac{1}{2},\ \frac{1}{2},\ 0)$	at	(.5000, .5000, .0000)
$(0,\ 2y,\ \frac{1}{2})$	at	(.0000, .2130, .5000)
$(\frac{1}{2},\ \frac{1}{2},\ 2z+\frac{1}{2})$	at	(.5000, .5000, .0000)

giving

(x, y, z)	at	(.0000, .1065, .2500) .

The general point (2x, 2y, 2z) appears at (.0000, .2130, .5000), coinciding with the Harker line point identified as $(0, 2y, \frac{1}{2})$, and

the ruthenium atom lies in a special position on a 2-fold axis at $(0, y, \frac{1}{4})$. Atoms in this special position are located at $\pm(0, y, \frac{1}{4})$ and $\pm(\frac{1}{2}, \frac{1}{2}+y, \frac{1}{4})$, producing C-centring of the heavy-atom lattice which leads to systematic weakness of all reflections having $h+k = 2n+1$, as only the light atoms contribute to this class of reflections. In an attempt to calculate phases for these systematically weak reflections, which clearly cannot be phased using the ruthenium position, the direct methods program DIRDIF.A [115] was used, but only a small number of the weak reflections were phased by the program, and the attempt was abandoned in favour of trial-and-error methods. A difference Fourier map was calculated using the ruthenium position, and two of the symmetry-related pairs of peaks which appeared were assigned as chlorine atoms and were used to break the pseudo-symmetry arising from the centring of the ruthenium atoms. Two further difference Fourier maps revealed that the remaining octahedral coordination positions around the ruthenium were occupied by a chlorine atom and a molecule of carbon monoxide, disordered about the 2-fold axis, and two $[PhCH_2PPh_3]^+$ cations and two molecules of dichloromethane, related by the axis, were also located. Least-squares refinement of the structure, with anisotropic temperature factors assigned to the ruthenium and the four ordered, coordinated chlorine atoms, and all the other atoms isotropic, converged at $R = 0.083$, after the application of a weighting scheme of the form $W = 1/(\sigma_F + 0.001|F_{obs}|)$, where σ was based on counting statistics.

A(iv) Results and Discussion

Structure factors and atomic coordinates for the two structures are given in Tables A.1 and A.2; bond distances and angles are given in Table A.3. The geometry and numbering scheme is shown in Figures A.1 and A.2 for the anions and the cation respectively.

The anion $[RuCl_3(CO)(C_7H_8)]^-$ is essentially octahedral, with a facial arrangement of chloride ligands, as predicted from the n.m.r. studies[129]. The effect of the diene ligand on the geometry of the anion is similar to that found in trans-$Ru(C_7H_8)(PhNH_2)_2Cl_2$,[130] where Ru-X is 2.066Å and X-Ru-X is 70.0° (X represents the middle point of a double bond in the diene); the corresponding values in the anion are Ru-X = 2.132Å (av.) and X-Ru-X = 69.5°. No other complex with chlorides cis to a coordinated norbornadiene molecule has been examined by X-ray diffraction, but in cis-$Ru(C_8H_{12})(CO)(MeCN)Cl_2$[131] there are two chlorides trans to coordinated cyclooctadiene. In this case the complex is less distorted from octahedral geometry due to the larger ligand bite of the diene (X-Ru-X = 84.4°), and the Cl-Ru-X angle of 175.6° and mean Ru-Cl distance of 2.395Å are rather different from the values found in the anion, viz. Cl-Ru-X is 165.7° and Ru-Cl is 2.426Å. No doubt the substantial deviation from trans-Cl-Ru-X geometry accounts for the greater Ru-Cl bond lengths.

The carbonylpentachlororuthenate(III) anion has been reported and studied by a number of investigators. $[NH_4]_2[Ru\ Cl_5(CO)]$[132] has been isolated from an aqueous solution of $[NH_4]_3[RuCl_6]$ containing 1-7 mol dm^{-3} HCl, after treatment with carbon monoxide, and $Cs_2[RuCl_5(CO)]$[133,134] was formed as the first product in the reaction of ruthenium trichloride in formic acid-HCl mixtures. The carbonyl stretching frequencies of these salts are given in Table A.4, and it is clear that the frequency is sensitive to the nature of the counterion. Extended reaction of ruthenium trichloride in formic acid/HCl leads to the formation of

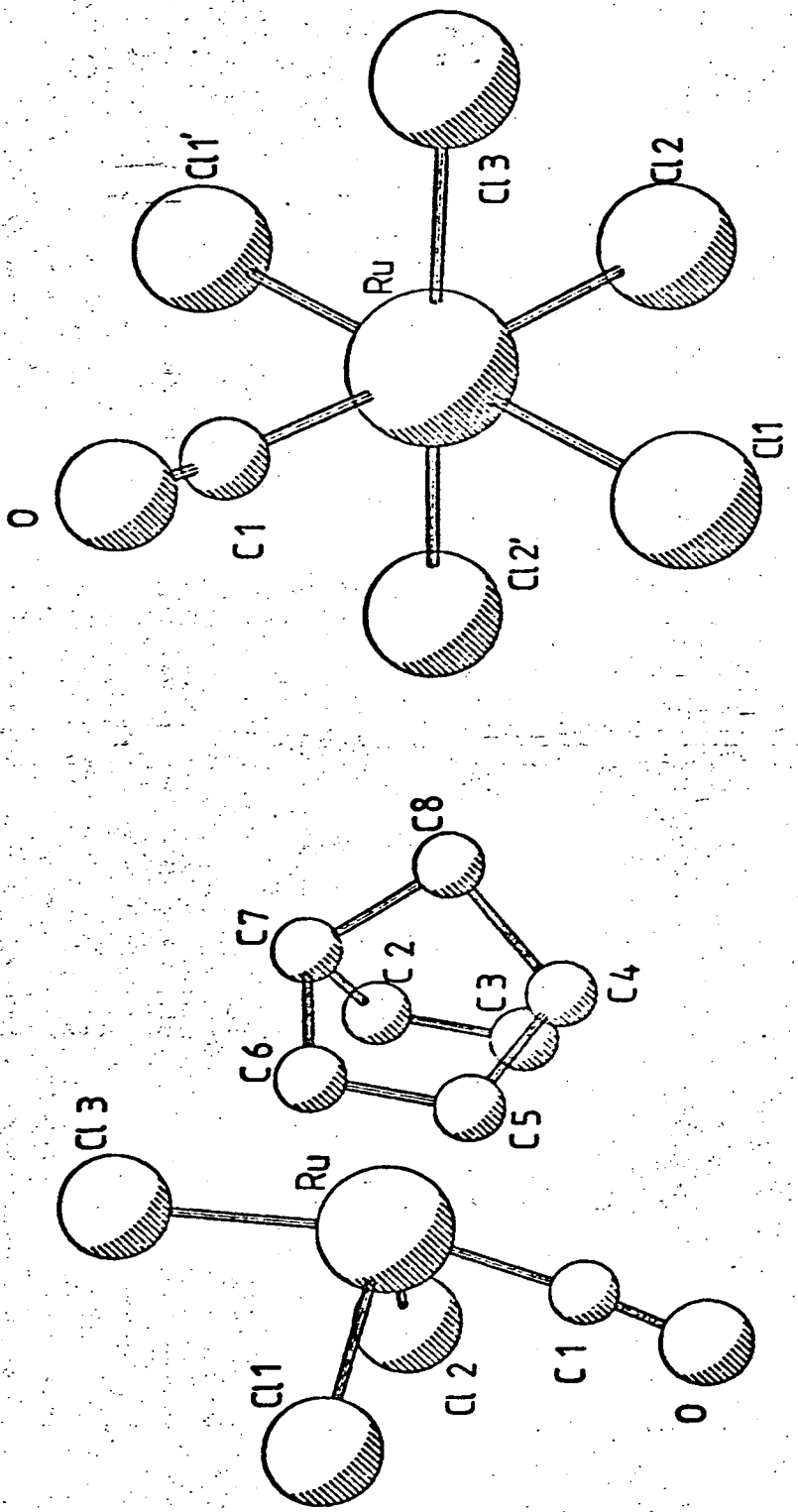
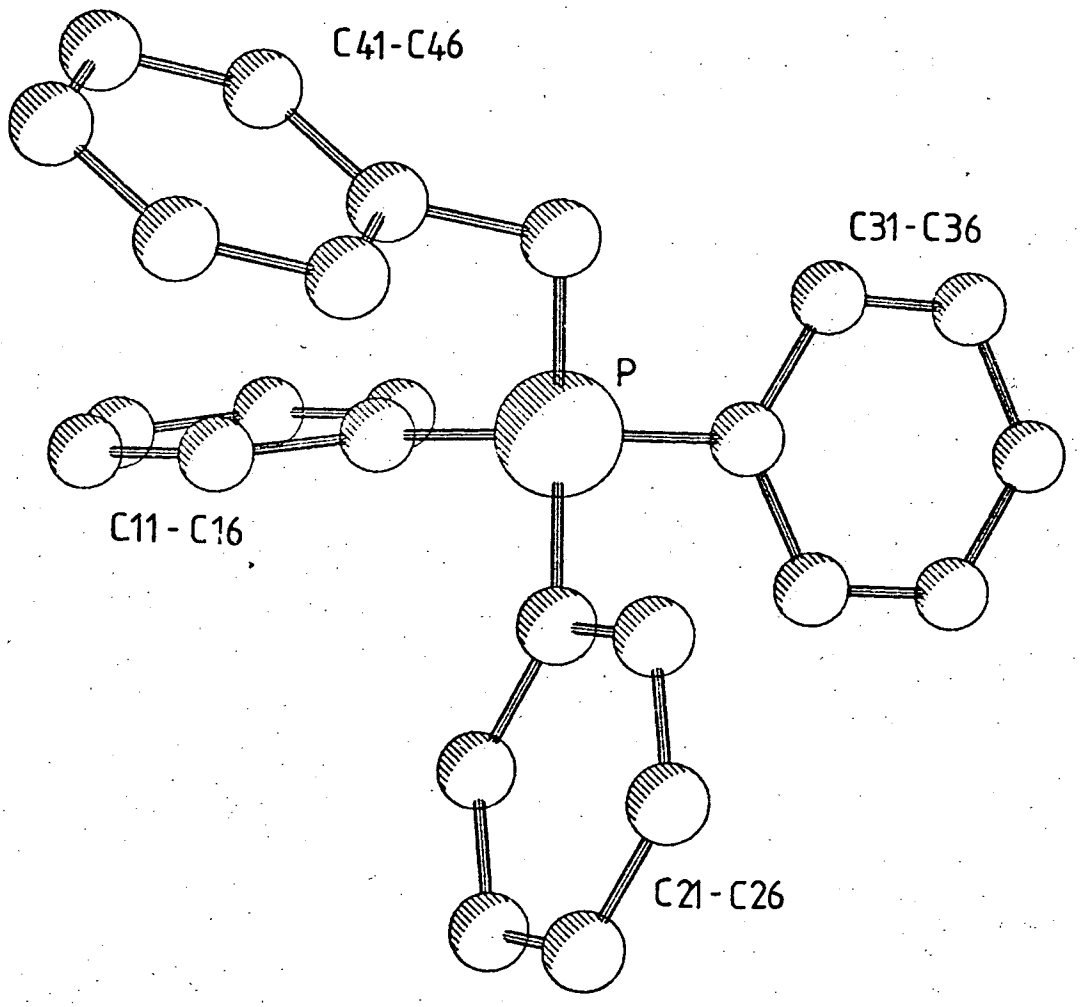


Figure A.1 Molecular structure and numbering scheme of $[RuCl_3(CO)(C_7H_8)]^-$ and $[RuCl_5(CO)]^{2-}$ anions.

Figure A.2 Molecular structure and numbering scheme of $[PhCH_2PPh_3]^+$ cation



green $[RuCl_4(CO)(H_2O)]^{2-}$, then orange $[RuCl_4(CO)_2]^{2-}$ and finally pale yellow $[RuCl_3(CO)_3]^-$ anions. Similarly, in the present work, further precipitation after the removal of $[PhCH_2PPh_3]_2[RuCl_5(CO)]$ led to the recovery of a material exhibiting several bands in the carbonyl stretching region, at 2016(w), 1994(s) and 1950-1930(s, broad)cm^{-1}. Comparison of these values with those in Table A.4 indicates that the final product is a mixture containing the $[RuCl_5(CO)]^{2-}$, $[RuCl_4(CO)(H_2O)]^{2-}$ and cis-$[RuCl_4(CO)_2]^{2-}$ anions.

Previous attempts to examine the $[RuCl_5(CO)]^{2-}$ anion by X-ray crystallography have not been successful. A preliminary study of $Cs_2[RuCl_5(CO)]$ [135] showed that the anion was required to have m 3 m symmetry (O_h), implying that the carbonyl group was completely disordered over six sites, and the work was not pursued further. In the present case, the crystallographic 2 (C_2) symmetry causes the carbonyl group to be disordered over two sites and the parameters determined are thus of low accuracy, with the C, O and C "half atom" appearing considerably closer together than the resolution of the data (apparent C-Cl = 0.67Å, Cl-O = 0.56Å). However, the Ru-Cl(1) distance (trans to Cl) of 2.374Å compares reasonably well with that found in $Cs_2[RuCl_5(H_2O)]$, where the unique bonds of the anion lie along a crystallographic 2-fold axis, and there is no disorder.

The major product of the reaction, $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$, is clearly formed by simple cleavage of the bridged dimeric starting material by chloride ions, retaining the facial arrangement of chloride ligands. The Ru(III) anion, interestingly, is apparently formed by reaction of the Ru(II) diene anion with concentrated HCl and excess chloride ion. This is evident from the fact that the reaction of $[RuCl_2(CO)(diene)]_2$ (diene = C_7H_8 or C_8C_{12}) with excess

$PhCH_2PPh_3Cl/HCl$ in acetone under reflux gave much higher yields of $[PhCH_2PPh_3]_2[RuCl_5(CO)]$, and no anionic diene complexes were isolated. It is worth noting, however, that the product obtained is very sensitive to the cation used, since the reaction of $[RuCl_2(CO)(C_7H_8)]_2$ with $AsPh_4/HCl$ in acetone under reflux gave $[AsPh_4]_2[RuCl_4(CO)_2]$.[128] Presumably, $[RuCl_5(CO)]^{2-}$ is formed initially, then undergoes reduction with abstraction of the additional CO group from the solvent (see refs. 133 and 134). A related example of the synthesis of a Ru(III) anion by reaction of a Ru(II) compound with MCl/HCl is the formation of $[AsPh_4][RuCl_4(PPh_3)_2].2Me_2CO$ by the reaction of $RuCl_2(PPh_3)_3$ or 4 with excess $AsPh_4Cl/HCl$ in acetone.[137] Although the detailed mechanism of this oxidation process is unknown, it is possible that Ru(IV) hydride intermediates are involved.

Finally, Berch and Davison have shown that the red solution made by passing CO through an ethanolic solution of "$RuCl_3.3H_2O$" contains some of the Ru(II) and (III) chlorocarbonyl anions discussed in refs. 133 and 134. They also present evidence that the $[RuCl_2(CO)(diene)]_2$ complexes are formed by the reaction of diene with the $[RuCl_5(CO)]^{2-}$ anion.[138] Hence it seems that the unusual reaction scheme shown in Scheme A.1 is applicable, involving reduction of Ru(III) by reaction with the diene and then oxidation of Ru(II) by MCl/HCl.

EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany and the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the region 4000-250 cm^{-1} on a Perkin Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Conductivity measurements were made on a Portland electronics conductivity bridge (model 310) and m.p.'s were determined with a Kofler hot-stage microscope and are uncorrected.

Benzyltriphenylphosphoniumcarbonylpentachlororuthenate(III)-dichloromethane

A suspension of the complex $[RuCl_2CO(C_7H_8)]_2$ (1.0g) was shaken in degassed acetone (100 cm^3) under nitrogen for 5 days with an excess of benzyltriphenylphosphonium chloride (2.8g) and concentrated hydrochloric acid (1.0 cm^3). The resulting orange $Ph_3PhCH_2P[RuCl_3CO(C_7H_8)]$ $\overset{1}{\sim}$ was filtered off and purified as described elsewhere[128]. Concentration of the remaining dark red solution under vacuo gave more of the anion $\overset{1}{\sim}$. After filtering off this product, the solution was further concentrated and then a mixture of dichloromethane - light petroleum (bp 110 - 120°C) was added to precipitate the red crystalline solid mp 230°C (but at 120-125°C, loss of solvent occurs) (Found: C, 53.6; H, 4.1, Cl 18.7, P, 6.7. Calc. for $C_{53}H_{48}Cl_9OP_2Ru$: C, 53.8; H, 4.1, Cl, 27.0 P, 5.2%. However Calc. for $[Ph_3PhCH_2P]_2[RuCl_5CO]$, Cl, 17.5; P, 6.1%). Mull i.r. spectrum: ν_{CO} 1994 cm^{-1}, ν_{RuCl} 320 cm^{-1} [Λ(0.001 mol. dm^{-3}) in CH_2Cl_2 = 26.0S cm^2 $mol.^{-1}$]

On leaving the solution to stand, more reddish-brown solid was precipitated. The i.r. spectrum (Nujol mull) showed several carbonyl bands at 2016w, 1994 and 1950 - 1930 cm^{-1} attributed to $[RuCl_5(CO)]^{2-}$ the Ru(II) anions mentioned in the text.

$[PhCH_2PPh_3]_2[RuCl_5(CO)]$ was also prepared by refluxing $[RuCl_2CO(diene)]_2$ (0.10g) (diene = C_7H_8, C_8H_{12}) in degassed acetone under nitrogen with Ph_3PhCH_2PCl (0.28g) and conc HCl(0.30 cm^3) for ca 4h. Concentration of the solution and addition of CH_2Cl_2 - light petroleum (bp 110-120°C) gave a red precipitate. (Found: C, 53.1, H, 4.1%) ν_{CO} 1994 cm^{-1} (nujol).

Table A.1a: Structure factors for $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$

Columns are l, $10|F_o|$, $10|F_c|$.

0.0.L

2	2955	2639
4	522	670
6	1636	1551
8	1117	1116
10	272	242
12	1128	1159
14	831	765

0.1.L

1	694	655
2	1412	1486
3	319	226
4	467	376
5	231	217
6	150	147
7	729	719
8	327	304
9	324	317
10	623	556
12	657	644
13	263	173

0.2.L

0	967	924
1	380	386
2	1061	1022
3	117	60
4	633	502
5	949	889
6	1576	1494
7	861	816
8	1116	1068
11	442	446
12	436	473
13	576	602

0.3.L

1	1123	1155
2	114	57
4	471	360
5	1030	940
6	423	384
7	231	212
8	355	297
9	264	219
10	249	295
11	513	469
13	317	351

0.4.L

0	980	951
1	2466	2549
2	1189	1122
3	261	260
4	502	440
5	1264	1594
6	261	268
7	1910	1829
8	476	455
9	619	596
11	259	280
12	153	116
13	516	561

0.5.L

1	926	868
2	1395	1390
3	630	675
4	269	267
5	788	775
6	333	342
7	264	245
8	263	233
9	650	621
10	321	302
11	571	561
12	411	415
13	496	472

0.6.L

0	773	825
1	149	157
3	1156	1123
4	1027	976
5	449	469
6	1369	1369
7	903	859
8	933	936
10	152	157
11	376	435
12	341	385
13	250	264

0.7.L

1	615	650
2	319	331
3	506	625
4	881	857
5	273	261
6	826	817
7	569	535
10	288	291

0.8.L

0	1304	1341
1	649	641
2	1361	1371
3	248	262
4	359	385
5	315	329
6	674	667
7	372	406
8	700	701
9	327	299
10	363	409
12	668	702

0.9.L

1	352	370
3	268	346
4	734	811
6	224	194
9	674	646
10	466	492
11	463	477
12	327	298

0.10.L

0	660	639
1	1188	1176
2	761	769
3	751	771
5	522	509
6	638	647
7	923	908
8	656	660
11	254	259

0.11.L

3	414	461
4	381	371
5	572	586
6	271	285
7	183	213
9	361	348
11	178	151

0.12.L

0	106	81
1	519	513
2	693	714
3	179	159
4	404	367
5	867	936
7	756	740
8	330	366
9	378	393
10	361	355

0.13.L

3	476	514
4	447	455
5	270	287
8	479	444
10	464	506

0.14.L

0	305	314
1	607	590
2	460	447
3	286	314
6	730	731
7	310	330
8	444	448

0.15.L

2	334	333
3	462	506
4	358	354
5	306	278
6	158	148
8	185	181

0.16.L

0	996	974
2	399	393
4	298	285
5	272	298
6	445	458
7	376	378

0.17.L

2	427	433
3	507	501
4	438	448
5	215	210

0.18.L

0	383	367
1	515	493
2	155	138
4	177	137

0.19.L

1	234	253

1.0.L

0	1129	1212
2	1329	1246
-2	1603	1557
4	152	95
-4	1225	1135
6	536	523
-6	669	577
8	722	635
-8	142	72
10	776	739
12	1104	1086
-12	712	630
-14	370	324

1.1.L

1	634	613
-1	1073	1101
2	3359	3401
-3	1366	1329
4	938	969
-4	2872	2662
-5	403	377
6	181	110
-6	1725	1665
7	351	312
-7	419	400
8	527	591
-8	663	617
9	881	782
-9	153	175
10	614	601
-10	732	711
-11	286	290
12	164	153
-12	886	882
13	180	208
-13	382	370
-14	449	472

1.2.L

1	1294	1257
-1	1726	1920
-2	1184	1258
3	373	295
-3	1857	1795
-4	184	213
-5	155	158
-6	969	884
-7	617	565
8	247	210
-8	549	547
9	269	170
-9	330	313
10	560	593
-10	459	436
11	270	745
-11	304	307
12	614	573
13	422	427
-13	178	141
-14	375	324

1.3.L

0	1027	1124
1	1790	1826
-1	1177	1173
2	273	296
-2	1140	1151
3	877	823
-3	75	107
4	332	220
-4	83	65
5	141	379
-5	1730	1673
6	527	546
-6	219	254
7	786	777
-7	420	437
8	816	770
9	1083	1072
10	488	473
-10	495	505
11	516	521
-11	562	539
12	148	179
-12	66	69
-13	530	530
-14	166	178

1.4.L

0	260	253
1	985	931
-1	465	378
2	672	644
-2	329	311
3	716	719
-3	321	325
-4	433	399
5	1011	995
-5	1432	1279
6	184	149
8	409	358
-8	1016	997
9	272	241
-9	393	371
-10	570	582
11	184	196
12	436	447
-12	291	277
-13	422	424

1.5.L

0	535	533
1	261	234
-1	101	120
2	523	527
-2	97	113
3	1224	1211
-3	389	406
-4	1004	994
5	163	128
-5	1563	1543
6	193	173
-6	313	326
7	748	714
-7	1077	1053
8	560	542
9	295	259
-9	112	87
10	457	453
-10	175	174
11	194	168
-11	546	584
12	214	214
-12	153	165
13	281	318
-13	580	595

1.6.L

0	902	956
1	1950	1923
-1	512	536
2	329	318
-2	451	484
3	209	199
4	1209	1156
-4	573	552
5	1589	1526
-5	360	349
6	593	616
7	670	660
-6	408	512
-7	575	543
-7	571	537
8	409	358
-8	1016	997
9	272	241
-9	393	371
-10	570	582
11	184	196
12	436	447
-12	291	277
-13	422	424

1.7.L

0	1502	1513
-1	441	464
2	1572	1590
-2	413	403
3	547	527
-3	330	335
4	357	359
-4	453	432
-5	148	158
6	796	794
-6	894	923
7	727	706
-7	533	525
8	1020	1017
-8	493	436
10	469	492
-10	554	566
-12	815	807

1.8.L

0	806	847
1	973	900
-1	238	187
2	145	162
-2	1298	1322
3	1116	1111
-3	179	163
4	282	315
-4	265	310
5	408	382
6	641	620
-6	184	170
-7	548	571
-8	316	282
10	318	316
-10	447	431
12	569	531
-13	161	178

1.9.L

-1	254	252
2	289	304
-2	159	173
3	993	993
-3	814	779
4	279	317
-4	350	364
5	307	309
-5	707	776
6	470	430
-6	1181	1165
7	144	160
-7	577	522
-8	521	519
9	406	369
-10	166	138
-11	218	203
-12	608	678

1.10.L

0	273	287
-1	793	790
2	202	161
-2	160	163
3	228	227
-3	760	773
4	379	380
-4	361	340
5	627	691
-5	590	526
6	770	779
7	166	171
-7	260	250
8	105	104
-8	214	221
9	462	455
-9	402	404
-10	153	131
11	515	507
-12	213	198

1.11.L

0	540	538
1	646	645
-1	275	331
3	269	217
-3	413	414
4	236	217
-4	517	522
-5	664	657
-6	271	251
7	1055	1055
-7	663	671
8	131	152
-8	365	394
9	636	655
-9	264	277
-10	133	119
11	213	246
-11	856	880

1.12.L

0	216	224
1	161	160
-1	625	651
2	343	377
-2	201	234
-3	314	353
4	140	171
-4	205	192
5	703	755
6	119	98
-6	469	478
7	422	468
-7	649	637
8	251	295
-8	175	208
-9	591	625
-11	361	365

1.13.L

1	374	349
-1	377	387
2	500	439
-2	261	267
3	235	244
4	515	542
-4	413	437
-5	361	332
-6	502	486
7	264	202
-7	201	207
8	287	275
9	344	340
-9	139	147

1.14.L

0	241	240
-1	272	277
2	225	237
-2	276	264
4	737	759
-4	265	216
5	113	105
-5	179	196
6	708	705
-6	364	394
7	215	239
8	136	145
-8	394	388

1.15.L

0	454	449
-1	229	231
2	670	679
3	261	258
-3	253	253
4	303	312
-4	668	694
-5	330	352
6	246	240
-6	594	592
7	270	279
8	401	494
-8	180	174
-9	196	205

1.16.L

0	554	554
-1	220	227
2	178	170
-2	705	680
3	155	143
4	179	162
-4	329	340
5	432	467
6	247	251
-6	261	293
-7	367	393
-8	274	275

1.17.L

0	442	409
1	360	362
-1	152	151
2	313	278
-2	171	153
3	204	214
-3	291	310
-4	243	227
-5	439	428
-6	181	160

1.18.L

0	145	178
-1	479	468
-2	180	132
3	279	287
-3	487	500

1.19.L

-1	166	163

2.0.L

0	270	275
2	1446	1795
-2	2065	2153
4	396	328
-4	2152	2114
6	200	213
-6	1225	1147
8	871	868
10	1324	1273
-10	739	697
12	390	434
-12	406	412
-14	151	157

2.1.L

0	2941	3048
1	584	593
-1	714	724
2	860	831
-2	1671	1720
-3	166	116
4	205	205
-4	347	338
5	272	204
-5	785	799
6	1427	1361
-6	1217	1185
7	455	401
-7	945	930
8	1469	1372
-8	945	892
-9	131	138
10	272	215
-10	361	338
11	349	376
-11	393	361
12	631	660
-12	624	625
13	415	414
-13	205	247
-14	429	434

2.2.L

-1	986	987
2	539	544
-2	1219	1286
3	267	153
4	220	255
-4	326	255
-5	1461	1403
6	543	556
-6	111	130
7	231	247
8	441	414
-8	357	369
9	309	312
-9	172	156
-10	581	503
11	477	463
12	237	206
-12	250	292
13	267	220

2.3.L

1	408	467
2	346	343
-2	250	204
3	313	306
-3	394	396
4	640	606
-4	697	666
5	672	617
-5	1586	1505
6	665	581
-6	549	537
7	1456	1337
-7	1693	1639
8	148	157
-8	336	320
9	415	432
-9	365	350
-10	148	131
11	436	448
-11	530	492
-12	484	483
-13	524	545
-14	220	249

2.4.L

1	639	634
2	834	776
3	977	926
-3	515	572
-4	389	363
5	1220	1111
-5	404	431
6	229	262
-6	353	293
7	323	301
8	118	78
-8	557	564
9	663	607
-9	922	892
10	435	409
-10	243	227
11	468	515
-11	812	836
-13	705	648
-14	249	237

2.5.L

0	1430	1423
-1	1127	1149
2	210	168
-2	932	913
3	576	543
-3	516	461
4	405	350
5	1003	1018
-5	610	807
6	799	630
-6	1051	1072
7	1210	1133
-7	770	754
8	459	477
-8	320	352
9	897	860
-10	206	193
-11	443	462
12	351	369
-12	238	240
-13	569	539
-14	229	251

2.6.L

0	1271	1243
1	561	529
-1	560	567
2	1667	1636
-2	255	213
-3	680	672
-5	738	767
6	1104	1127
-6	355	402
-7	109	147
-8	159	83
9	776	753
-9	325	345
10	142	119
-10	383	389
-11	239	264
-12	556	531
13	254	246
-13	412	440
-14	125	119

2.7.L

0	1298	1301
1	556	580
-1	208	350
2	1009	1056
-2	463	404
3	570	552
-3	182	171
4	535	553
-4	728	724
-5	711	717
6	670	660
-6	1005	1018
8	408	422
-8	1234	1195
9	258	259
-9	189	152
10	240	245
-10	168	145
12	510	543
-12	602	620
-13	263	264

2.8.L

0	691	705
1	97	88
-1	727	737
2	758	780
-2	1038	1049
3	178	164
-3	319	317
4	633	644
-4	807	814
5	103	136
-5	221	199
-6	931	914
-7	249	238
-8	436	401
-8	317	307
9	226	194
-9	546	539
10	398	429
-10	547	589
-11	351	333
-12	511	488
-13	133	141

2.9.L

0	1640	1654
1	759	807
-1	1318	1333
2	1222	1232
-2	615	620
-3	274	257
4	762	768
-4	175	183
5	593	546
6	966	969
-6	579	573
7	578	568
-7	370	366
8	533	516
-8	619	616
9	231	229
-9	256	269
-10	169	181
-11	138	147
-12	478	483

2.10.L

0	226	225
-1	609	582
2	415	383
3	746	787
-3	982	1032
4	126	156
-4	242	241
-5	281	259
6	434	429
-7	327	340
8	229	225
9	477	467
-9	389	352
-10	521	521
11	436	442
-11	395	394
-12	621	625

2.11.L

0	284	297
1	868	858
-1	555	575
2	132	97
-2	453	438
3	204	203
-3	513	492
4	139	112

2.12.L

0	445	440

Table A.1a continued

2,11,L

5	400	401
-5	865	862
6	333	333
-6	195	207
7	526	521
-7	685	644
8	257	269
9	342	354
-9	367	364
10	143	129
-11	265	260
-12	129	145

2,12,L

0	466	465
1	392	415
-2	606	611
-3	454	466
-4	251	247
5	755	757
-5	367	369
6	184	195
-6	216	199
7	281	235
-8	121	141
9	175	143
-11	351	333

2,13,L

0	608	590
1	593	577
-1	451	475
2	493	507
-2	372	375
-3	129	124
4	356	351
-4	142	153
5	421	442
-5	725	752
6	225	213
7	424	432
-7	640	630
8	234	227
-8	250	259
9	233	248
-9	164	163

2,14,L

0	152	176
1	126	157
-1	197	141
2	367	373
-2	394	379
3	152	196
4	561	624
-4	335	335
-5	431	437
6	146	102
7	143	164
-8	454	461
-10	622	634

2,15,L

0	417	398
1	112	86
-1	233	235
2	516	512
-2	389	394
3	254	232
-3	316	317
-4	267	249
5	139	135
6	496	476
-6	532	513
-9	269	277

2,16,L

1	522	541
-2	296	266
3	639	635
4	384	364
-4	672	641
5	355	364
6	248	242
-6	242	232
-7	145	136

2,17,L

0	346	358
1	337	344
-1	319	306
2	145	155
-4	262	267
5	132	131
-5	151	171
-6	659	663

2,18,L

-1	243	227
-3	584	567
-4	129	103
-5	437	416

3,0,L

0	597	625
2	1208	1239
-2	1993	2059
4	996	982
-4	1118	1144
6	648	659
-6	2275	2237
8	668	688
-8	993	1003
10	565	528
-10	429	427
12	173	202
-12	473	470

3,1,L

0	1262	1312
1	702	701
-1	203	232
2	569	585
-2	135	55
3	230	243
-3	1234	1237
4	577	548
-4	262	235
5	188	214
-5	630	628
6	968	928
-6	460	443
-7	345	327
8	145	140
-8	788	807
-9	580	572
10	501	485
-10	363	367
-11	103	139
12	573	602
-12	315	323
-13	314	297
-14	417	423

3,2,L

0	880	899
1	380	432
-1	279	284
2	1045	1056
-2	642	625
-3	137	103
-4	553	553
5	503	420
-5	1892	1860
6	549	483
-6	1145	1096
7	1350	1288
-7	950	974
8	633	606
-8	525	472
9	1090	1038
-9	340	329
10	221	240
-10	605	592
-11	938	924
-12	839	722
-13	499	516
-14	371	383

3,3,L

0	89	97
1	642	651
-1	657	720
2	536	629
-2	941	959
-3	403	454
4	294	264
-4	112	102
5	1330	1276
-5	104	116
6	160	172
-6	107	50
-7	803	779
8	643	628
-9	675	660
10	288	303
-10	275	271
11	629	593
-12	225	233
-13	137	152

3,4,L

0	156	143
1	1871	1923
-1	893	900
2	536	492
-3	349	394
4	911	851
-4	289	281
5	535	514
-5	861	880
-6	861	848
7	334	323
-7	409	475
-8	161	175
-9	749	671
-10	156	162
-11	715	743

3,5,L

0	627	655
1	593	585
-1	839	869
-2	247	199
3	312	303
4	271	282
-4	435	461
5	768	779
-5	820	793
6	626	626
-6	206	213
7	654	651
-7	983	958
8	266	246
-8	674	692
9	242	247
-9	289	294
10	353	350
11	320	322
-11	238	221
12	220	186
-13	147	179
-14	149	118

3,6,L

0	1064	1070
1	897	922
2	1477	1485
-2	322	330
3	250	309
-3	784	834
4	451	422
-4	462	464
-5	877	897
6	389	366
-6	756	805
-7	467	500
8	777	732
-8	167	145
9	189	228
-9	181	201
10	353	325
-10	830	841
11	303	290
-12	914	943
-13	349	361
-14	440	448

3,7,L

0	1230	1266
1	278	247
-1	443	439
2	339	346
-3	120	49
4	939	932
-4	629	635
5	210	200
-5	437	396
6	582	566
7	156	135
-7	327	323
-8	616	627
9	171	195
-9	266	243
10	369	336
-10	336	348
-11	136	124

3,8,L

0	1010	1006
1	753	751
-1	155	190
2	1126	1148
3	399	374
4	162	153
-4	1444	1443
5	389	400
-5	271	277
6	651	623
-6	1156	1155
7	200	180
-7	312	315
8	756	754
-8	303	317
10	520	525
-10	273	321
-12	783	779

3,9,L

0	714	713
1	236	240
-1	439	502
-2	1071	1043
3	575	612
-3	97	81
4	309	310
5	197	185
-5	475	453
6	286	260
-6	653	629
7	337	305
-7	456	442
-8	320	327
-9	333	331
10	259	269
-10	361	392
-11	139	195
-13	243	252

3,10,L

0	988	1008
1	561	535
2	875	912
-2	205	223
3	236	270
-3	922	939
4	358	384
-4	660	691
5	265	316
-5	735	739
-6	717	722
7	493	456
-7	550	569
8	159	158
-8	409	426
9	570	532
-9	128	167
-11	278	274
-12	398	397

3,11,L

0	397	395
1	523	499
-1	1255	1242
2	241	242
-2	512	567
3	427	452
-3	776	767
4	248	229
-4	320	304
5	625	712
6	381	371
-6	182	181
7	541	515
-7	447	428
-8	159	135
9	263	209
-9	473	478
-11	429	410

3,12,L

1	742	763
-1	487	503
2	161	163
-2	353	347
3	311	333
-3	389	410
4	220	260
-4	549	560
-5	431	448
7	442	445
8	162	135
9	473	492
-9	234	247
-10	148	138
-11	723	700

3,13,L

1	364	357
-1	571	540
2	343	327
-2	319	323
-3	519	529
4	391	404
5	478	447
-5	285	311
6	306	266
-6	512	510
7	591	578
-7	205	209
-8	284	291
-9	235	212
-10	120	119

3,14,L

0	542	522
2	651	612
3	264	244
4	541	555
-4	316	283
-5	471	521
-6	492	494
7	204	221
-7	342	321
-8	122	132

3,15,L

0	456	435
-1	232	242
-2	482	445
3	239	262
-3	140	135
4	469	438
-4	337	335
6	523	535
-6	179	159

3,15,L

-6	1037	1047
7	227	220
-7	142	167
8	552	548
-8	496	492
9	639	629
-9	399	390
10	169	190
-10	896	882
11	416	435
-11	172	124
-12	663	711
-14	143	141

3,16,L

0	378	391
-1	168	178
-2	630	632
-3	969	959
4	304	323
-4	1237	1267
-5	476	504
6	144	133
-6	660	633
7	131	142
-8	299	299
9	442	426
-9	327	295
10	398	397
-10	601	632
-11	154	192
-12	664	708
-13	165	175

3,17,L

0	460	536
-1	217	225
2	387	422
-2	218	175
3	139	161
-3	312	311
4	130	95

3,18,L

1	222	217
2	130	147
-3	225	199

4,0,L

0	1099	1134
2	275	238
-2	804	785
4	736	734
6	1039	1002
-6	1392	1388
7	1024	1060
-8	935	942
10	185	190
-12	211	235
-14	242	249

4,1,L

0	268	245
1	376	316
-1	358	435
2	738	762
3	422	436
-3	544	557
4	369	376
-4	1242	1252
5	509	490
-5	339	297

4,3,L

1	1392	1387
-1	744	759
2	435	403
3	1343	1341
-3	319	252
4	259	276
5	731	667
-5	484	568
6	235	226
-6	514	449
7	275	236
-7	324	337
8	113	109
-9	490	525
10	381	352
11	391	364
-11	908	911
-13	251	238

4,4,L

0	392	421
1	1681	1736
2	172	114
-2	151	163
3	423	438
-3	213	254
-4	849	824
5	345	328
-5	770	767
6	626	598
-6	234	228
7	1126	1061
-7	682	707
8	266	270
9	462	466
-9	153	162
11	227	196
-11	768	779
-12	275	253
-13	694	729

4,5,L

0	841	800
1	442	449
2	297	336
-2	403	434
3	543	547
-3	1285	1349
4	660	617
-4	731	755
5	367	357
-5	856	923
6	528	515
-6	223	231
7	206	190
8	475	476
-8	553	575
9	317	290
-9	411	410
10	369	334
-10	612	602
11	271	278
-11	761	763
-13	592	614

4,6,L

0	1084	1177
1	572	562
8	534	524
9	585	589
-10	462	483
-12	474	487

4,11,L

0	239	265
1	737	751
-1	116	65
-2	83	81
3	526	547
-3	634	660
-4	177	204
5	477	433
-5	134	120
6	173	160
7	198	199
9	400	390
-9	339	323
-10	180	195
-11	339	313
-12	185	139

4,12,L

0	110	127
1	928	912
-1	921	965
2	277	265
-2	151	160
3	726	723
-3	273	271
-4	238	273
-5	954	977
7	417	412
-7	933	901
8	186	202
-8	436	434
-9	173	166
-11	243	248

4,13,L

1	487	483
-1	437	446
-2	573	554
3	518	546
4	245	252
-4	729	741
5	214	235
-5	376	366
6	174	153
-6	167	158
-7	246	234
-8	208	196
-9	178	159

4,14,L

0	716	694
1	529	563
2	561	543
-2	464	485
3	152	149
-3	416	394
5	197	223
-5	241	252
6	477	475
-6	423	420
7	292	295
-7	148	122
-10	155	153

4,15,L

0	199	237
1	224	237
-1	376	402
2	460	451
-2	367	389
3	230	221
4	446	425
-4	363	378
5	194	184
6	108	120
-6	320	272
-7	249	218
-8	121	117
-9	253	272

4,16,L

0	283	228
-1	326	319
2	473	450
-3	240	228
-4	227	188
-5	136	162
-6	670	668

4,17,L

0	178	185
-1	208	207
2	249	227
-2	217	245
3	254	233
-3	482	473
-4	154	191
-5	331	322
-6	239	256

4,18,L

0	197	173
-1	257	240
-2	132	124

5,0,L

0	602	676
2	271	288
-2	229	246
4	278	293
-4	736	719
6	680	668
-6	665	689
8	307	272
-8	1168	1163
10	310	289
-10	1145	1138
-12	264	298

5,1,L

0	892	940
1	521	549
-1	312	346
2	1493	1559
-2	400	419
-3	398	444
-4	1366	1416
5	275	287
6	355	366
-6	831	863
7	554	534
-7	621	601
8	524	497
-8	621	599
9	270	314
-9	159	176
10	558	558
-10	497	498
-11	638	628
-12	562	525
-13	286	276
-14	344	306

5,2,L

0	470	518
1	401	399
-1	1005	1036
2	389	372
-2	996	1014
3	1173	1171

Table A.1a continued

5.2.L

-3	322	347
4	510	515
-4	358	379
5	963	943
-5	176	139
6	245	246
-6	331	314
7	521	489
-7	253	246
8	172	163
-8	214	237
9	484	470
-9	269	302
10	249	274
-10	359	389
-11	207	221
-12	265	261
-14	246	229

5.3.L

0	437	414
1	1635	1717
2	146	99
-2	163	191
3	860	892
-3	1253	1247
4	416	385
5	215	196
-5	1437	1495
-6	725	724
7	504	466
-7	376	402
8	367	346
-8	239	246
9	527	534
-9	624	605
10	327	283
-10	575	601
-11	963	1011
-12	561	535
-13	225	229

5.4.L

0	636	656
1	948	979
-1	1181	1237
-2	264	284
-3	462	449
-4	1247	1221
5	526	499
6	539	481
-6	95	64
7	620	619
-7	355	416
8	111	96
-8	715	723
-10	256	227
-13	175	193

5.5.L

0	553	547
1	1168	1215
-1	462	494
2	1001	1033
-2	186	156
3	1282	1317
-3	258	289
4	354	318
5	409	385
-5	759	803
6	241	221
-6	281	303
7	171	160
-7	484	493
-8	371	345
9	691	675
-9	353	336
10	201	163
-10	359	372
-11	420	439
-12	216	250
-13	396	332
-14	228	206

5.6.L

0	1190	1230
-1	246	262
2	339	323
-2	997	1033
-3	297	302
4	407	397
-4	921	938
5	321	310
-5	269	259
7	274	301
-7	621	622
8	184	196
-8	291	267
-9	190	219
10	139	139
-10	135	159
-11	441	402
-14	464	463

5.7.L

8	589	572
-8	243	240
-9	260	259
-10	298	317
-12	404	428

6.10.L

-1	114	144
2	106	111
-2	448	463
3	666	720
-3	150	128
4	190	150
-4	626	653
5	570	569
-5	270	268
6	357	371
-6	424	429
7	209	208
-8	230	224
-9	756	775
-10	145	132
-11	540	520
-12	321	356

6.11.L

1	828	820
-1	714	738
3	759	803
-3	155	147
-4	137	135
5	244	243
-5	610	613
-6	144	114
7	588	573
-7	826	811
-8	266	261
-9	335	336
-10	277	262
-11	363	347

6.12.L

1	183	195
-2	142	172
3	416	451
-3	230	222
4	369	393
-4	152	199
-6	213	214
-8	129	171
-9	315	327
-10	199	210
-11	462	442

6.13.L

0	267	253
1	979	991
-1	675	630
2	461	462
-2	132	98
3	291	275
4	206	219
-5	483	486
-6	299	303
-7	277	231
-8	449	446
-9	138	111

6.14.L

0	208	206
1	159	192
2	157	177
-2	469	466
3	128	164
-3	285	267
4	430	426
-4	591	619
-6	467	477
-8	125	141

6.15.L

0	587	561
2	360	323
-2	337	389
3	223	215
-3	368	383
-4	383	385
-5	318	320
-6	595	593
-8	359	351

6.16.L

1	173	159
-1	115	150
-2	156	181
-3	278	251
-4	149	169
-5	142	131

7.0.L

0	1501	1537
2	1147	1177
-2	581	573
4	600	615
-4	897	918
-6	738	732
8	702	749
-8	405	409
-10	1025	1017
-12	803	829
-14	329	333

7.1.L

0	422	456
1	135	118
-1	184	171
2	174	156
-2	768	797
3	386	392
-3	138	145
-4	494	473
5	424	446
-5	558	549
6	532	539
-6	689	689
7	557	577
8	333	334
-8	855	843
9	256	244
-9	132	166
-10	600	591
-11	415	422
-12	335	324

7.2.L

0	299	309
1	661	722
2	430	439
-2	341	357
3	438	444
-3	676	704
4	284	283
-4	1192	1199
5	322	340
-5	1039	1042
-6	681	678
-7	477	513
8	587	587
-9	451	447
-9	508	514
-10	403	402
-11	548	569
-12	283	322
-13	294	313
-14	147	161

5.12.L

-2	349	301
-3	303	277
-4	192	206
-5	134	149

5.17.L

1	315	305
-2	394	382
-4	409	379
-5	316	299

6.0.L

0	664	665
2	660	690
-2	1260	1282
4	579	577
-4	1314	1367
6	270	308
-6	466	457
-10	783	785
-12	350	299
-14	137	151

6.1.L

0	1115	1127
1	837	864
-1	495	503
2	239	277
-2	385	407
3	106	114
-3	284	249
4	165	144
-4	688	729
5	212	222
-5	221	252
6	769	801
-6	1271	1255
7	313	305
-7	351	350
8	799	798
-8	379	387
9	238	242
-9	562	545
10	245	291
-10	274	242
-11	134	109
-12	422	447
-14	479	509

6.2.L

0	355	342
1	1396	1333
-1	271	297
2	575	575
-2	109	130
3	692	731
-3	231	316
4	275	279
-4	737	799
5	238	280
-6	440	432
-7	931	953
8	317	326
-8	276	270
9	267	242
-9	600	634
10	431	408
-10	466	466
-11	664	666
-12	412	397
-13	373	347

6.3.L

0	776	782
1	1448	1491
-1	1239	1275
2	1043	1103
-2	677	695
3	483	490
-3	223	232
4	447	433
-4	317	314
-5	1307	1326
6	153	164
-6	364	397
7	619	617
-7	456	469
-8	534	512
9	719	691
10	215	179
-10	362	276
-11	361	343
-12	313	291

6.4.L

-1	656	658
2	304	325
-2	515	537
3	640	666
-3	1304	1368
-4	438	478
5	329	322
-5	938	976
6	106	89
-6	187	212
7	224	238
-7	562	550
8	316	305
-9	377	376
-10	254	257
-11	599	598
-13	133	135

6.5.L

0	611	618
1	1103	1112
-1	467	522
-2	102	53
3	487	475
-3	127	121
-5	320	351
6	253	226
-6	272	254
7	705	730
-7	889	909
9	366	353
-9	216	262
-10	169	180
-11	647	679
-12	223	224
-13	566	572
-14	240	218

6.6.L

0	369	360
1	106	96
2	247	246
-2	717	759
3	488	514
4	229	235
-4	894	938
5	489	462
-5	554	619
6	182	196
-6	318	321
-7	327	298
8	186	180
-8	434	449
9	120	155
-9	366	381
-10	529	530
-11	469	428
-12	364	353
-13	112	130

6.7.L

0	457	462
1	170	155

7.3.L

0	228	226
1	366	393
-1	777	798
2	269	272
-2	324	349
3	317	347
-3	658	673
4	260	230
-5	554	546
-5	401	380
-6	346	357
7	524	568
-7	377	404
-8	338	349
-9	679	662
-10	146	122
-14	222	232

7.4.L

0	258	271
1	1047	1112
-2	647	658
3	977	1007
-3	786	791
4	137	153
-4	155	141
5	154	132
-5	1105	1127
6	184	213
7	484	484
-7	614	612
8	193	186
-8	139	155
-9	562	592
-11	932	921
-12	243	229
-13	518	433

7.5.L

0	432	449
1	597	628
-1	761	812
-2	425	441
4	158	167
-4	299	299
5	275	260
-6	418	382
7	162	126
-7	465	484
8	219	230
-8	168	177
-9	511	525
-11	335	331
-13	134	130

7.6.L

0	128	131
1	790	821
2	236	240
-2	566	605
-3	403	429
4	120	127
-4	555	557
-5	387	390
6	258	207
-6	1081	1004
7	415	413
-7	201	192
8	518	528
-8	459	515
-9	224	210
-10	236	222
-11	570	528
-12	161	179
-13	237	234

7.7.L

0	262	254
-2	463	470
3	351	370
-3	239	249
4	754	746
-4	194	150
5	375	338
6	668	662
-6	143	144
-7	163	164
8	279	270
-8	562	535
-10	312	328
-11	257	293

7.8.L

0	473	478
1	277	282
-1	312	311
2	299	291
-2	421	446
-3	272	277
4	617	632
6	333	337
-6	653	646
-10	513	519
-12	732	744

7.9.L

0	349	369
1	293	312
-1	569	573
-2	121	159
3	202	223
-3	119	118
4	337	333
-4	146	154
5	154	167
6	356	320
-6	209	193
7	159	166
-7	394	402
-8	430	431
-9	516	510
-10	491	522
-11	335	318

7.10.L

0	420	422
1	714	716
-1	117	142
2	499	496
-2	216	212
3	602	616
-3	304	283
4	169	162
-4	242	266
5	149	154
-5	224	210
6	253	221
-6	140	140
-7	256	265
-9	160	161
-11	505	522
-12	227	236

7.11.L

-1	398	413
2	253	256
-2	217	207
3	331	306
-3	275	267
4	466	469
-4	270	289
5	677	694
-5	172	193
6	167	196
-8	225	229
-9	173	138
-10	159	150
-11	243	228

7.12.L

1	467	440
-1	131	133
2	541	538
-2	123	120
3	504	557
-3	861	843
-4	119	118
5	129	107
-5	798	765
-6	111	118
-7	343	339
-9	177	164
-10	246	256

7.13.L

0	730	737
-1	369	349
2	234	259
-2	423	411
3	130	150
-3	436	451
4	204	219
-6	127	138
-8	467	449
-9	238	250

7.14.L

1	204	177
-2	473	448
-2	315	335
3	291	287
-3	262	247
-4	381	371
-5	426	438
-6	359	346

7.15.L

0	202	221
-1	161	158
-2	306	311
-4	261	223
-8	195	225

7.16.L

-3	159	153
-4	596	593

Table A.1a continued

8,0,L

0	182	181
2	642	649
4	256	259
-6	322	326
-8	540	545
6	540	545
-6	216	227
8	546	553
-8	355	346
-10	325	311
-12	447	455
-14	379	366

8,1,L

0	127	116
1	227	231
-1	218	194
2	583	577
-2	315	296
3	243	235
-3	153	130
4	792	769
-4	1157	1156
5	275	270
-5	309	319
6	499	509
-6	486	492
8	184	162
-8	213	224
-9	239	213
-10	666	673
-11	431	436
-12	440	445
-13	163	139

8,2,L

0	395	410
1	935	928
-1	640	650
2	341	347
-2	200	212
3	766	802
-3	623	626
4	161	167
-4	560	579
-5	334	329
6	179	189
-6	504	491
7	561	576
-7	507	502
-9	250	276
-10	287	257
-11	452	427
-12	343	337
-13	189	206
-14	242	247

8,3,L

-1	432	439
-2	673	692
3	515	552
-3	631	636
-4	303	296
5	537	558
-5	172	199
6	307	322
-6	117	113
-7	317	350
-8	266	262
-9	265	272
-10	327	320
-11	577	584
-12	370	366
-13	165	119

8,4,L

0	465	457
1	676	728
2	143	169
-2	147	153
3	197	218
-3	396	401
5	413	424
-5	606	630
-6	214	207
7	636	646
-7	699	725
-8	419	427
-9	320	301
-10	124	111
-11	255	251
-13	293	252

8,5,L

1	311	293
-1	457	447
2	184	186
3	723	746
-3	225	234
4	304	287
-4	735	737
5	233	222
-5	617	613
-6	576	582
-7	405	406
-8	261	254
-9	272	267
-10	471	488
-11	544	523

8,6,L

0	673	681
1	506	533
-1	373	420
2	587	596
-2	349	333
-3	486	477
-4	179	204
5	335	358
-5	453	436
6	552	527
-6	852	840
-7	255	269
-8	475	455
-11	302	292
-12	123	122
-13	353	340

8,7,L

1	309	316
-1	150	144
2	544	555
-2	694	703
3	533	546
-3	156	134
4	424	413
-4	471	483
-5	124	140
-8	542	535
-9	394	430
-10	666	685
-11	336	365
-12	696	673

8,8,L

0	676	677
1	279	293
-1	246	271
2	263	280
3	109	102
-3	123	123
-4	425	425
-5	263	273
6	252	243
-6	347	336
-12	237	240

8,9,L

0	406	433
1	297	294
2	509	476
-2	360	355
3	691	713
-3	436	453
4	470	470
-4	470	463
5	367	358
-5	242	272
-6	205	225
-9	161	170
-10	245	229
-11	194	179
-12	420	411

8,10,L

1	840	878
-1	866	874
3	206	233
-4	523	560
5	241	237
-5	287	299
-6	377	379
-7	210	177
-9	130	111
-10	138	147
-11	223	237

8,11,L

1	277	313
-1	512	499
3	460	444
-3	656	612
-4	394	393
-5	171	170
-6	305	273
-7	154	142
-8	238	229
-9	393	410

8,12,L

0	279	259
1	542	537
-1	462	457
3	234	245
-4	101	146
-5	314	275
-6	132	112
-7	302	310
-9	181	161

8,13,L

0	137	161
-1	134	123
2	235	262
-2	579	562
-3	433	385
-4	327	315
-5	337	332

8,14,L

0	305	311
-4	389	418
-5	253	263
-6	518	489
-7	270	261

8,15,L

-2	378	360
-4	493	493

9,0,L

0	993	1003
2	470	427
-2	1142	1169
4	213	222
-4	376	407
6	497	521
-8	586	594
-10	600	610
-12	168	158

9,1,L

0	244	222
1	409	439
-1	300	302
2	542	547
-2	122	107
3	621	622
-3	270	267
4	377	366
-4	379	408
5	318	344
6	236	266
-6	341	316
-7	392	394
-8	232	214
-9	98	85
-10	665	678
-11	497	483
-12	389	392
-13	170	152

9,2,L

0	219	190
1	340	348
-2	252	231
3	287	295
4	257	275
-4	239	244
5	544	508
-5	204	263
6	402	420
-7	239	230
-8	535	529
-9	499	485
-10	332	319
-12	129	133
-13	314	329

9,3,L

1	618	635
2	145	162
-2	536	535
3	752	767
-3	401	413
-4	568	574
5	155	135
-5	727	695
-6	107	96
-7	665	601
-8	127	76
-9	172	159
-10	204	223
-11	482	487
-12	156	119
-13	206	193

9,4,L

0	314	343
1	487	497
-1	891	929
2	284	291
-2	127	121
3	302	300
-3	424	428
4	196	184
-4	203	172
5	446	453
-6	247	252
-7	380	352
-8	560	565
-9	719	741
-11	225	192
-13	194	171

9,5,L

1	592	600
2	279	239
-2	394	328
3	506	568
-3	647	671
4	234	233
-4	253	253
-5	306	614
6	225	224
-6	489	458
-7	212	221
-8	265	294
-9	699	713
-10	363	366
-11	693	682
-12	374	378
-13	357	363

9,6,L

2	300	304
-3	447	443
4	463	492
5	162	154
-5	165	192
-6	381	384
-7	413	425
-8	565	573
-9	206	181
-10	306	329
-11	213	213

9,7,L

0	536	521
1	374	386
-1	348	353
2	635	625
-2	173	223
3	192	211
-3	179	201
4	281	274
-4	876	862
5	277	265
-5	192	181
-6	642	609
-8	117	144
-10	183	207
-11	203	178
-12	236	236

9,8,L

0	552	542
1	165	184
-1	476	467
2	231	231
-2	774	770
-3	245	258
4	303	306
-6	412	405
-7	122	117
-8	249	223
-9	262	247
-10	364	379
-11	144	132

9,9,L

0	506	524
1	404	356
-1	349	371
2	523	512
3	130	132
4	266	285
-4	606	600
-6	240	240
-8	380	401
-9	119	145
-10	373	350
-11	278	253

9,10,L

1	152	133
-1	553	548
-2	412	405
-3	537	548
-4	273	273
-7	413	419
-8	145	144
-9	185	168
-10	320	306

9,11,L

1	446	430
-3	554	530
-5	809	797
-7	192	202
-9	156	166

9,12,L

1	104	86
-1	399	366
-2	355	346
-3	338	362

9,12,L

-8	119	123
-9	583	571
-10	367	344
-11	585	578
-12	381	367

9,13,L

0	221	213
-1	133	154
-3	377	342
-4	159	161
-5	537	560
-6	104	101
-7	264	247

10,0,L

0	359	356
2	957	979
-2	349	357
4	467	454
-4	574	592
-6	242	225
-8	165	173
-10	300	279
-12	346	375

10,1,L

0	597	610
1	536	560
-1	317	306
2	614	616
-2	339	352
3	148	174
-3	239	230
-4	555	569
-6	621	636
-7	268	283
-8	264	229
-12	361	374

10,2,L

0	171	155
1	156	164
-1	804	791
2	239	262
-2	272	244
3	463	465
-3	396	379
4	221	202
-4	448	428
-5	572	565
-6	276	292

10,3,L

0	135	134
1	856	897
-1	271	259
2	124	140
-2	165	195
3	229	215
-3	142	88
-4	336	342
-5	329	322
-6	122	139
-7	465	480
-8	115	135
-9	113	102
-11	404	399

10,4,L

0	333	343
1	443	448
2	328	361
3	599	592
-3	659	648
-4	206	210
-5	467	479
-7	165	171
-8	411	595
-11	544	536

10,5,L

0	466	467
1	343	355
-1	158	149
2	142	122
-2	165	146
-3	234	235
-4	271	282
-4	334	336
-5	568	547
-6	326	325
-7	682	693
-8	120	76
-11	269	273
-12	119	107

10,6,L

0	234	246
1	177	191
2	474	480
-2	459	446
3	311	322
-3	475	446
-4	389	360
-5	443	452
-6	161	181
-8	499	496
-9	462	473
-10	645	671
-11	327	325

10,7,L

0	456	449
-1	416	451
2	505	491
-2	497	474
3	168	181
-3	162	135
-4	190	174
-6	406	403
-8	206	225
-10	238	308

10,8,L

0	222	267
-2	491	467
-4	709	695
-8	515	489
-9	192	224
-10	523	495

10,9,L

0	294	279
1	273	288
-1	305	317
2	328	328
-2	161	162
-3	115	111
-4	166	187
-5	489	498
-6	381	365
-7	355	362
-8	153	153

10,10,L

0	125	123
1	119	126
-2	153	136
-3	559	545
-4	233	214
-5	536	571
-9	292	245

10,11,L

-1	478	502
-2	181	169
-4	324	360
-5	402	396
-6	136	146
-7	386	363

10,12,L

-3	634	626
-4	153	138
-5	269	270

11,0,L

2	278	277
-2	451	455
-4	835	850
-8	367	322
-10	534	515

11,1,L

0	471	457
1	133	114
-1	411	395
2	165	172
-2	741	743
-3	493	467
-4	358	336
-5	281	257
-7	173	180
-8	324	312
-9	169	171
-10	488	498

11,2,L

0	205	206
1	697	694
2	339	344
-2	285	287
3	399	401
-3	644	652
-4	392	404
-5	336	294
-7	216	215
-9	181	161

11,3,L

-1	430	421
3	333	307
-3	226	230
-5	142	128
-6	334	347
-7	348	319
-8	293	280
-9	459	450
-10	216	195
-11	174	173

11,4,L

0	120	97
1	340	313
2	138	160
-3	472	453
-4	262	266
-5	656	666
-6	197	213
-7	162	157
-9	390	372
-11	518	499

11,5,L

0	214	217
1	208	210
-1	513	484
-2	389	362
-3	499	494
-5	321	323
-6	420	400
-7	360	326
-8	295	301
-9	605	602
-10	123	98

11,6,L

0	324	303
1	194	225
-1	134	100
2	581	596
-2	316	306
-4	331	310
-5	371	375
-6	249	193
-7	143	155
-9	310	298
-10	373	385

11,7,L

0	165	156
1	219	243
-2	176	156
-5	143	151
-6	296	284
-7	166	191
-8	567	475

11,8,L

0	247	237
-2	134	129
-4	423	410
-6	550	523
-7	144	170

11,9,L

-1	372	340
-2	426	406
-3	507	517
-4	389	376
-5	211	190
-7	175	176
-8	346	303

11,10,L

-3	264	275
-4	218	235
-5	404	402

12,0,L

0	449	476
-2	152	124
-4	490	498
-6	822	834
-8	290	265

12,1,L

-2	366	330
-3	393	365
-4	389	348
-5	411	430
-6	125	85
-8	427	409
-9	176	169
-10	309	264

12,2,L

0	386	380
-1	402	370
-2	122	151
-3	134	129
-4	158	203
-5	283	274
-6	349	335
-7	288	283
-8	293	270

12,3,L

-1	364	361
-3	690	641
-5	544	561
-6	142	140
-7	231	173
-9	459	416

12,4,L

0	169	159
-1	253	207
-2	141	104
-4	171	172
-5	414	358
-6	249	226
-7	437	433
-8	123	18

12,5,L

-1	209	208
-3	288	284
-4	184	173
-7	159	113
-8	378	357

12,6,L

-1	214	204
-2	146	158
-5	144	117
-6	231	207
-7	271	259

12,7,L

-3	257	256
-4	466	435
-5	229	232
-6	207	225

13,0,L

-4	446	388
-6	190	151

13,1,L

-4	513	494
-5	338	326
-6	368	320

Table A.16: Structure factors for $[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$.

Columns are 1, $10|F_o|$, $10|F_c|$. Negative F_o represents "unobserved reflection".

0,0,L

4	2272	2405
6	514	546
10	1346	1386
12	1053	994
14	938	912
16	1038	1063
18	636	657
20	597	644

0,2,L

0	2341	1891
1	2037	2036
2	673	791
3	2765	2658
4	2107	2269
7	1251	1367
9	662	657
10	751	811
11	930	890
14	-214	272
15	852	728
17	568	525
18	361	388
19	580	496

0,4,L

0	5086	4284
1	327	379
2	717	644
4	-84	43
5	707	862
6	677	659
7	1410	1661
8	1038	1108
9	2079	2298
10	1081	1343
11	796	881
12	925	1030
13	1203	1479
14	883	965
16	-248	200
17	-136	24

0,6,L

0	935	797
1	974	1033
2	253	267
3	955	961
5	1616	1766
6	1132	1242
7	-199	332
8	974	1086
9	2205	2425
10	1362	1512
11	1163	1252
12	921	1043
13	1243	1352
16	-134	229

0,8,L

1	751	814
2	862	841
3	1262	1219
4	762	700
5	837	834
7	783	757
8	636	706
9	502	530
10	635	637
11	1064	1005
12	466	523
13	312	271
14	665	753
15	944	937

0,10,L

0	2465	2237
1	-41	353
2	1426	1381
3	853	871
4	1782	1822
6	353	329
7	289	132
8	517	454
10	425	362
11	468	425
12	1320	1281
14	360	512

0,12,L

0	1090	914
1	1355	1329
2	-242	186
3	1161	1151
4	-280	366
6	346	335
8	735	772
10	466	420
11	726	623
13	600	558

0,14,L

0	344	447
2	1355	1336
3	-163	5

1,1,L

5	466	461
6	676	730
10	873	865
12	627	577

1,3,L

0	924	796
1	733	723
3	486	586
4	358	378
5	349	469
7	432	461

1,5,L

1	1455	1296
2	1997	2022
3	986	989
4	1861	2061
7	545	408
8	426	503
9	481	549
10	861	864
12	1083	1148
13	939	1006
14	484	365
16	-313	386
17	480	413
19	-95	172
20	347	279

1,7,L

0	656	578
1	2207	2097
2	1503	1612
3	2922	3089
5	460	506
6	950	1114
7	1217	1233
8	994	1122
9	1335	1229
10	716	674
11	1134	1256
12	530	589
13	968	1278
15	472	448
18	-264	269
19	-258	291

1,9,L

1	733	683
4	1652	1753
5	497	502
6	700	758
9	675	733
19	-218	94

1,11,L

0	1645	1575
2	698	672
3	609	553
4	815	850
7	359	486
8	1506	1767
9	654	725
10	1335	1372
12	1434	1503
14	532	524
16	324	325
19	-146	36

1,13,L

1	1776	1614
2	555	592
3	699	700
5	380	504
6	336	395
9	317	304
11	583	610
18	-90	233

1,15,L

0	918	786
1	1741	1718
2	970	936
3	1332	1125
5	1325	1355
6	-283	264
7	1133	1161

1,17,L

0	1201	1151
1	1821	1721
2	540	508
3	1024	1033
4	-203	211
5	457	534
8	418	371
9	-128	197
11	390	351
12	500	487
14	395	381
15	-261	289

1,19,L

1	-114	129
4	427	363
7	316	332
8	447	438

1,21,L

0	1822	1775
2	1125	1119
3	565	525
4	377	359
7	553	454
9	575	561

1,23,L

1	-114	56
3	-57	135
7	-163	185

1,25,L

0	-219	263
3	600	574
4	468	548
5	-264	224
8	772	655
10	474	575

1,27,L

1	360	368
2	-269	225
3	320	345
4	-231	153
5	361	291
6	-129	88

1,29,L

0	508	611
1	543	554
5	578	557

2,0,L

0	4518	4248
4	2713	2655
6	556	525
8	364	354
10	477	426
12	1089	1013
14	559	587
16	605	459
18	682	577

2,1,L

3	395	478
4	1978	2100
5	2082	2177
6	2045	2020
7	339	419
8	1115	1036
9	719	691
11	673	584
12	568	614
13	971	976
14	575	617
16	422	422
17	574	630

2,2,L

0	1173	1146
1	2567	2093
2	1919	1598
3	1559	1566
5	1575	1767
6	1077	1203
7	817	841
9	634	643
10	817	808
11	1154	1160
13	336	280
15	960	1000
19	675	567

2,3,L

1	1207	1045
2	235	132
3	2467	2297
4	1344	1281
5	683	685
6	885	854
7	-95	236
8	760	780
11	-159	170
12	-215	165
13	-209	296
14	424	377
15	-155	32
19	-150	117

2,4,L

0	584	500
1	1441	1174
2	2711	2408
3	851	792
4	985	1034
5	1042	999
6	1128	1236
9	669	632
10	1299	1496
13	775	831
14	743	752
17	684	648

2,5,L

1	932	685
2	2124	2001
4	2954	3007
6	788	901
9	515	453
10	354	353
14	311	358

2,6,L

0	521	426
1	723	665
2	613	580
4	571	598
5	1833	1870
6	319	356
8	874	974
9	1136	1178
10	692	721
11	603	554
12	655	574
13	762	844

2,7,L

1	1186	1129
3	943	833
5	1484	1428
8	755	737
9	604	565
10	-297	118
12	353	237
13	-159	125

2,8,L

0	948	759
1	874	868
2	1741	1632
3	1384	1127
5	493	559
6	744	832
7	825	980
8	438	427
10	962	1333
11	948	1161
12	329	250

2,9,L

2	-72	111
4	1016	1053
5	-242	229
7	-246	290
8	663	635
15	-153	295

2,10,L

0	1840	1800
1	577	521
2	557	630
3	408	411
4	1180	1261
7	434	432
8	935	1055
11	-289	334
12	810	773

2,11,L

1	521	468
3	-121	151
8	-276	404
9	-186	368
12	-105	108
13	481	451

2,12,L

0	601	534
1	1370	1301
3	876	927
4	544	592
5	570	570
7	677	657
9	514	455
13	390	344

2,13,L

9	-243	168
13	-61	160

2,14,L

2	1366	1315
3	312	293
4	-106	227
5	-262	330
6	828	548
7	-221	144
8	479	554
10	635	634

2,16,L

0	466	352
1	606	587
5	556	555
7	420	426

2,17,L

1	-256	159
2	484	463
4	352	339

3,0,L

2	1152	1166
6	1724	1574
10	1046	983
14	602	546
16	452	420
18	-152	153

3,1,L

0	3039	2951
1	1821	1635
2	1166	1149
3	2304	2262
5	1746	1744
6	1404	1372
7	711	725
8	1364	1327
9	1387	1270
12	626	486
14	643	602
15	-186	130
16	411	290
17	926	841
18	634	548

3,2,L

1	2825	2405
2	527	536
3	1245	1154
5	335	294
6	738	742
7	518	555
9	835	756
14	-129	27
15	450	516

3,3,L

0	1527	1250
1	508	409
2	385	342
3	1248	1223
4	454	430
5	647	573
6	1005	1105
7	935	1116
9	1021	974
11	721	663
13	-229	189
14	404	438
15	731	593
17	600	473
19	648	463

3,4,L

2	2929	2540
3	634	559
4	2693	2452
8	587	474
9	493	447
11	448	331
12	465	513

3,5,L

0	1853	1641
1	533	516
2	2024	1806
3	394	439
4	2106	2172
5	-257	313
6	1367	1347
8	2284	2253
12	672	731
14	536	538
15	-172	221
16	579	525
17	379	414
18	516	459

3,6,L

2	955	906
3	1463	1381
4	475	427
5	658	720
6	646	739
7	809	826
8	380	378
9	505	443
14	-292	140
15	-98	245
17	362	391

3,7,L

0	1724	1610
1	816	693
2	593	532
3	842	896
4	695	694
5	921	1012
6	-125	137
7	1015	1139
8	521	533
9	761	789
10	405	448
11	439	427
13	-279	342
15	547	721

3,8,L

2	1323	893
4	383	398
7	668	651
9	428	392
15	536	519
17	-263	259

3,9,L

0	833	687
1	705	695
2	1314	1335
3	389	353
4	628	595
5	-136	148
6	1554	1543
7	487	434
8	811	754
9	595	555
10	325	330
12	-259	293
14	587	519
16	-312	284

3,10,L

4	987	951
6	437	372
7	-266	296
8	584	537
9	-317	322
12	-122	296
14	599	634

3,11,L

1	544	459
3	719	712
4	661	653
5	1477	1518
7	810	865
9	935	956
10	-144	253
11	546	503

3,12,L

4	740	723
6	365	396
7	504	416
14	-271	330

3,13,L

3	606	663
6	806	867
7	490	574
10	622	572

3,14,L

3	328	257

3,15,L

0	1133	1056
1	-301	321
2	451	414
3	-247	332
4	903	980
5	362	459
7	468	486
8	498	579

3,16,L

3	432	479
4	-204	340
5	633	601
6	-226	32

3,17,L

0	434	388
1	419	435

4,0,L

0	2609	2535
2	2690	2733
4	1843	1563
6	1278	1246
8	3053	2853
10	1065	1015
12	1052	955
16	680	571

4,1,L

1	1058	1103
2	716	730
4	1318	1284
5	605	638
6	456	422
12	-187	288
14	-105	200
15	521	433

4,2,L

0	-162	133
1	412	366
2	1566	1459
3	1152	1211
5	2535	2581
6	1406	1506
7	2224	2357
8	-157	262
9	1405	1468
10	555	573
11	556	551
13	476	426
14	452	325
15	650	724
19	527	467

4,3,L

1	1134	1012
2	1026	950
4	556	566
8	552	639
12	411	465
14	430	427
17	-245	125

4,4,L

0	353	301
1	1013	885
2	1362	1206
3	437	475
4	1523	1520
5	1149	1124
6	1805	1761
7	430	533
8	752	816
9	533	648
10	640	753
11	434	354
14	375	375
16	804	785
17	861	808
18	508	421

4,5,L

1	507	532
2	973	869
4	385	416
5	431	420
6	873	777
8	299	285
10	742	840
13	-55	79
15	-36	43

4,6,L

0	2333	1892
1	868	748
2	1347	1128
4	978	972
5	1282	1202
6	795	803
9	432	390
11	540	526
14	647	621
17	979	822

4,7,L

2	386	316
3	1189	1087
5	917	813
16	-277	128

4,8,L

0	1162	1004
1	895	782
2	1207	1167
3	1681	1614
4	824	798
5	1271	1254
6	1210	1273
7	1238	1291
8	461	525
9	-141	41
10	357	241
11	832	873
14	441	268
15	586	497

4,9,L

1	575	537
3	-279	139
7	-244	335
11	-45	234
15	-98	117

4,10,L

0	1186	1039
2	639	554
3	721	551
4	992	1214
6	672	636
7	569	557
8	1193	1272
10	-333	222
11	-337	338
12	485	512
13	-138	15

4,11,L

1	601	545
5	497	515
7	-266	254
10	-333	131
14	-342	199

4,12,L

0	1361	889
2	849	759
3	1145	1089
5	899	971
7	1352	1397
8	572	557
9	869	934
10	371	393
11	526	492
13	-198	212

4,13,L

5	-270	258
6	613	495

4,14,L

2	1317	976
3	678	613
6	1137	1192
8	583	559
9	-88	44
10	366	391

Table A.1b continued

4,15,L

3	-224	78
4	-295	308

4,16,L

3	599	594
5	704	787

5,0,L

4	1011	1013
6	706	680
8	557	542
12	549	448
14	-270	332

5,1,L

0	808	743
1	735	643
2	617	614
3	1149	1177
4	1159	1161
5	1029	1053
6	1727	1892
7	1178	1158
8	978	1042
9	1096	1106
10	831	859
14	509	448
17	514	419
18	423	356

5,2,L

1	1253	1218
2	665	623
5	657	720
8	463	562

5,3,L

0	1327	1249
1	1044	903
2	828	837
3	1206	1176
5	1167	1206
6	792	818
7	1364	1514
10	-270	334
14	483	453
15	690	582
17	606	526
18	-346	229

5,4,L

1	875	759
2	354	201
6	473	445
8	311	327

5,5,L

0	2041	1937
1	265	228
2	1915	1858
3	1425	1253
4	2730	2551
5	505	465
6	515	520
8	852	887
9	465	504
11	-224	218
13	346	311
16	930	836

5,6,L

7	553	504
9	538	450
14	-317	349

5,7,L

0	1432	1248
1	515	442
3	1321	1152
4	736	721
5	1386	1205
6	675	662
7	1053	1013
9	723	673
10	426	453
13	416	305
15	492	445

5,8,L

1	502	448
3	467	330
9	-256	172
10	-276	2
12	-312	238

5,9,L

0	576	560
3	-215	57
4	1024	912
6	1613	1568
7	335	338
8	950	986
9	772	769
10	1047	989
12	451	488
13	524	487

5,10,L

3	377	371
4	-211	235
5	-169	226
6	-253	216
10	-258	308

5,11,L

3	-269	213
4	543	561
5	1148	1095
6	513	523
7	1172	1134
8	532	557
9	1381	1398
13	701	716

5,12,L

1	-202	287
3	408	352
4	-116	103
5	-164	117
7	-195	178
10	-58	24
11	-121	35

5,13,L

1	574	516
3	703	674
4	748	696

5,14,L

2	-203	249
8	-88	97

5,15,L

0	1070	1028
1	500	413
4	833	886

5,16,L

2	327	195

6,0,L

4	1683	1737
6	1645	1739
8	2287	2236
10	1357	1533
12	1193	1073

6,1,L

1	614	673
4	-227	116
7	443	534
8	822	817
13	718	642
17	-348	133

6,2,L

0	365	334
1	497	459
2	1076	1130
3	328	387
4	633	670
5	903	978
7	1527	1554
8	443	533
9	1321	1136
11	951	919
12	-283	352
15	935	894
16	-139	215

6,3,L

2	362	332
3	949	936
4	472	413
5	-155	29
8	507	614
9	345	246
11	-313	186

6,4,L

0	535	453
1	1199	1353
2	1271	1148
3	977	944
4	737	767
5	1390	1370
6	1644	1577
9	-321	432
10	545	472
13	-196	176
17	623	574

6,5,L

4	1061	904
5	738	620
6	613	553
7	543	456
8	491	511
9	-90	9
10	-292	269

6,6,L

0	1186	1040
1	2064	1920
2	1283	1207
3	1207	1151
4	523	499
5	718	781
6	511	555
8	-214	10
9	482	529
11	410	595
13	686	719
15	373	427
16	384	373

6,7,L

2	-90	115
3	1412	1272
5	522	508
6	561	455
9	-99	210
13	-353	391

6,8,L

1	780	609
2	1039	955
3	661	577
4	536	517
5	789	710
6	714	690
7	1011	973
9	-187	231
11	646	679
15	534	558

6,9,L

1	430	435
4	513	577
10	666	573
11	-281	92
13	-213	152

6,10,L

0	1013	946
3	366	315
4	1264	1158
5	-260	221
6	903	885
7	677	620
8	1157	1015
10	744	719
11	-230	249
12	636	658

6,11,L

6	-265	200
9	-201	202

6,12,L

0	318	181
3	744	683
4	656	585
5	872	838
7	926	918
8	552	585
9	721	762
10	-105	158

6,13,L

1	317	152
2	326	173
3	356	257
10	311	271

6,14,L

0	566	442
2	865	853
6	880	882

6,15,L

3	360	321
4	-162	38

7,0,L

2	-108	36
6	461	448
8	747	635
10	401	318
12	441	532

7,1,L

2	1442	1431
4	-234	293
5	635	689
6	876	876
8	965	952
9	956	1018
10	909	882
12	477	469
13	669	589
14	821	804

7,2,L

1	1028	1011
3	581	530
4	-29	139
5	-202	134
9	436	463

7,3,L

1	1681	1642
2	1348	1293
3	714	788
4	-207	242
5	1217	1180
6	740	768
7	990	999
10	960	991
11	842	926
13	452	489
15	586	552

7,4,L

2	1272	1164
3	663	675
4	1234	1243
6	454	511
8	-245	174
10	-310	359
11	-258	229
13	-190	5
14	-234	274
16	-189	150

7,5,L

0	1227	1023
1	339	176
2	1152	981
4	1118	1109
6	340	214
7	409	333
12	435	455
16	557	613

7,6,L

1	532	455
3	742	811
5	618	610
8	361	351

7,7,L

0	775	676
1	1839	1524
2	591	520
3	1333	1221
4	-337	229
5	915	860
6	761	737
7	634	638
9	-333	299
11	652	638

7,8,L

1	-56	30
2	449	414
5	541	446
6	-139	193
7	413	423

7,9,L

0	895	797
2	1191	1132
4	416	414
6	1332	1349
10	833	759
12	653	650

7,10,L

6	355	297
8	586	516

7,11,L

2	432	399
3	613	636
4	686	696
5	648	633
8	551	518
9	832	819

7,12,L

6	-217	177
8	-247	346

7,13,L

2	514	489
3	544	557
6	645	644
7	445	436

7,14,L

4	401	380

7,15,L

0	746	724

8,0,L

0	1521	1700
2	1358	1458
4	1304	1384
8	801	856
10	584	606
12	1132	978

8,1,L

3	763	719
4	-196	200
7	898	869
8	-234	270
11	-329	232
12	-260	183
13	558	461
14	481	365
15	524	381

8,2,L

0	638	607
1	1206	1272
2	661	634
3	1057	1067
6	342	299
8	-264	297
11	1340	1382
14	-193	138
15	577	542

8,3,L

2	671	607
3	714	663
5	446	440
6	396	393

8,4,L

0	1203	1232
1	758	720
2	1665	1625
5	720	762
6	661	655
9	957	934
10	415	354
12	584	544
13	592	535

8,5,L

2	961	951
4	643	613
6	548	566
12	545	571

8,6,L

1	1121	1021
2	617	614
3	1122	1036
4	515	455
5	555	560
9	569	548
10	626	646
13	653	650

8,7,L

3	610	661
5	770	774
10	-241	209

8,8,L

1	767	662
2	811	731
5	663	700
7	553	465
9	505	517
11	705	655
12	463	434
13	456	367

8,9,L

6	430	359
9	-264	133
12	-133	112

8,10,L

0	1600	1526
1	526	311
4	1086	1018
8	759	760
9	-301	293

8,11,L

6	-300	141
9	-237	199

8,12,L

1	972	917
2	430	305
4	575	551
5	462	451
7	406	351
8	547	465

8,14,L

0	618	612
2	699	653

9,0,L

4	726	775
6	-288	318
14	360	350

9,1,L

0	1180	1101
1	1038	1081
2	950	1038
9	841	862
10	629	622
12	619	659
13	554	569
14	485	418

9,2,L

3	520	548
4	-270	185
5	-303	321
11	408	284

9,3,L

1	1142	1185
2	600	527
3	627	649
6	528	560
7	718	743
10	575	657
11	719	823

9,4,L

3	636	665
5	654	588

9,5,L

0	1405	1335
1	451	253
3	-222	134
4	1347	1324
8	936	938
10	734	750
12	967	1031

9,6,L

4	332	247
7	387	337
9	-235	95

9,7,L

0	413	193
1	1115	1132
2	712	575
3	904	951
4	476	555
7	522	579
8	-222	232
9	544	457
11	745	749

9,8,L

5	619	373

9,9,L

0	1343	1140
1	531	633
2	1187	1372
3	597	636
4	609	634
10	562	612

9,11,L

1	959	955
2	524	629
3	728	723
5	-276	219

9,12,L

3	-333	133

10,0,L

0	1812	1897
2	1156	1245
4	959	1056
6	454	445
8	-130	270

10,1,L

2	354	363
5	-249	265
7	-129	37
8	-232	261
9	-121	174
12	-182	164

10,2,L

1	1290	1410
3	1023	1038
5	-304	211
6	557	558
7	657	665
10	611	590
13	570	570

10,3,L

1	541	502
9	-189	132

10,4,L

0	437	457
2	829	900
3	326	189
6	467	498
9	564	647
10	742	898
11	-270	421

10,5,L

10	-222	217

10,6,L

0	344	370
1	483	342
4	507	465
6	580	562
7	555	533
9	671	614
10	681	656

10,7,L

6	-170	121
7	-282	205

10,8,L

0	428	264
1	954	922
2	633	556
3	444	461
6	412	478

10,9,L

2	414	328
3	431	415

10,10,L

0	1155	1221
1	568	583
4	830	756

10,11,L

3	547	495

11,0,L

2	-366	414
4	655	647
8	-134	23

11,1,L

0	550	535
1	932	917
2	841	835
3	565	613
4	350	460
5	556	515
6	549	605

11,2,L

1	412	557
4	-190	15
5	414	430
9	-292	417
10	-235	196

11,3,L

2	672	710
3	621	578
5	-266	303
6	536	552
7	616	656
9	552	533

11,4,L

4	475	441

11,5,L

3	-162	192
4	837	853
8	1033	1136

11,7,L

3	521	509
5	499	534
6	-97	100
7	653	660

11,8,L

2	-183	99

11,9,L

1	428	406
2	928	911
3	352	146

12,0,L

0	756	852
2	554	579
4	744	832
8	533	555

12,1,L

2	-261	157
5	554	558
8	345	251

12,2,L

1	534	558
2	333	150
3	625	546
5	587	739
6	392	436
7	619	596

12,3,L

1	397	512
7	-212	34

12,4,L

2	617	556
4	-334	418
6	647	715

12,5,L

3	-242	233
4	436	548

12,6,L

0	610	660
5	553	548

13,0,L

4	353	399

13,1,L

1	473	433

TABLE A.2 Fractional coordinates ($\times 10^4$) for $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$ and $[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$

	$[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$			$[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$		
	x/a	y/b	z/c	x/a	y/b	z/c
Anion						
Ru	3784(1)	1833(1)	6772(1)	0	1063(1)	2500
Cl(1)	4803(2)	711(1)	7453(1)	1125(4)	1084(4)	1649(3)
Cl(2)	1894(1)	1297(1)	6078(1)	920(4)	2002(3)	3029(3)
Cl(3)	3396(2)	1951(1)	8345(1)	987(19)	177(15)	3106(12)*
C(1)	3938(6)	1505(4)	5601(5)	-752(35)	324(27)	2139(25)*
O	4032(5)	1246(3)	4885(5)	-1065(45)	1108(30)	1967(32)*
C(2)	3219(6)	2984(4)	6682(5)			
C(3)	3415(6)	2840(4)	5793(5)			
C(4)	4660(6)	3051(4)	5972(5)			
C(5)	5305(6)	2461(4)	6726(5)			
C(6)	5217(6)	2611(4)	7613(5)			
C(7)	4352(6)	3288(4)	7413(5)			
C(8)	4795(7)	3709(4)	6688(6)			
Cation						
P	9421(1)	1009(1)	2820(1)	9934(5)	2931(3)	127(3)
C(11)	9488(5)	1987(3)	3020(5)	10532(15)	3484(11)	-461(9)
C(12)	10463(6)	2377(4)	3078(5)	11394(20)	3208(14)	-740(12)
C(13)	10511(7)	3128(5)	3258(6)	11879(20)	3629(14)	-1168(12)
C(14)	9578(7)	3473(5)	3353(6)	11530(22)	4321(16)	-1331(13)
C(15)	8621(7)	3096(5)	3309(6)	10721(22)	583(15)	-1046(14)
C(16)	8558(6)	2347(4)	3136(5)	10154(19)	4159(11)	-606(11)
C(21)	8160(5)	795(4)	1774(4)	8804(14)	3341(10)	340(9)
C(22)	7694(5)	93(4)	1673(5)	8567(15)	3470(11)	964(10)
C(23)	6787(6)	-85(4)	814(5)	7680(18)	3783(12)	1093(11)
C(24)	6361(6)	425(4)	69(5)	7051(17)	3944(12)	597(11)
C(25)	6812(6)	1118(4)	162(5)	7266(17)	3798(12)	5(12)
C(26)	7722(6)	1312(4)	1021(5)	8164(16)	3467(12)	-164(10)
C(31)	10617(5)	688(4)	2505(5)	9682(15)	2023(11)	-192(10)
C(32)	10542(6)	682(4)	1498(5)	9711(16)	1894(11)	-831(11)
C(33)	11433(7)	408(5)	1233(6)	9470(19)	1190(14)	-1048(13)
C(34)	12390(6)	137(4)	1950(6)	9282(18)	675(13)	-634(12)
C(35)	12494(6)	156(4)	2952(6)	9252(20)	807(14)	-16(13)

Table A.2 (Contd.)

	$[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$			$[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$		
	x/a	y/b	z/c	x/a	y/b	z/c
C(36)	11608(6)	428(4)	3230(5)	9481(19)	1500(14)	235(12)
C(40)	9426(5)	540(4)	3954(5)	10734(18)	2818(13)	809(11)
C(41)	8538(5)	819(4)	4368(5)	11062(16)	3495(11)	1148(10)
C(42)	7420(6)	562(4)	4004(5)	10866(18)	3544(13)	1763(12)
C(43)	6622(7)	814(4)	4406(6)	11238(21)	4150(15)	2142(13)
C(44)	6940(7)	1325(5)	5169(7)	11732(20)	4676(14)	1837(14)
C(45)	8050(7)	1577(5)	5549(6)	11876(19)	4640(13)	1222(12)
C(46)	8842(6)	1327(4)	5160(5)	11583(18)	4046(14)	870(12)
			Solvent			
C(9)				3025(23)	2344(16)	2113(15)
Cl(4)				3855(7)	1641(5)	1953(4)
Cl(5)				3583(8)	2985(6)	2603(5)

* These atoms have a site occupancy of 0.5.

TABLE A.2 Contd.

Fractional co-ordinates ($\times 10^4$) of hydrogen atoms in $[PhCH_2PPh_3][RuCl_3(CO)C_7H_8)]$ and $[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$.

The atom given is that to which the hydrogens are joined.

	$[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$			$[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$		
	x/a	y/b	z/c	x/a	y/b	z/c
C(2)	248	290	683			
C(3)	285	264	516			
C(4)	484	302	533			
C(5)	577	204	661			
C(6)	543	233	825			
C(7)	427	348	806			
C(8)	432	416	636			
	562	389	699			
C(12)	1114	210	300	1164	272	-63
C(13)	1123	342	331	1248	345	-137
C(14)	960	403	347	1186	463	-166
C(15)	793	337	338	1051	509	-113
C(16)	785	206	310	953	433	-43
C(22)	801	-28	223	903	335	131
C(23)	643	-60	75	749	387	155
C(24)	571	30	-56	644	420	71
C(25)	648	150	-39	677	389	-33
C(26)	807	183	107	833	335	-62
C(32)	983	86	96	990	229	-114
C(33)	1138	41	50	944	109	-152
C(34)	1304	-7	174	916	17	-79
C(35)	1320	-3	349	906	40	28
C(36)	1166	42	395	948	160	70
C(40)	928	-1	380	1039	250	113
	1020	59	448	1132	256	65
C(42)	721	19	345	1048	316	197
C(43)	582	61	415	1112	419	261
C(44)	633	153	543	1200	510	208
C(45)	827	194	612	1222	506	100
C(46)	966	194	543	1175	402	41

TABLE A.2 (Contd.)

Temperature factors for $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$ (1) and $[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$ (2). All values are $10^3 \underset{\sim}{U}$ in $\AA^2$.

A. Anisotropic temperature factors.

	$\underset{\sim}{1}$						$\underset{\sim}{2}$					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	31	39	20	1	5	1	30	29	60	-	-1	-
Cl(1)	51	44	49	15	-4	3	41	52	73	7	6	-5
Cl(2)	31	50	52	-7	3	4	39	45	58	-3	-8	-5
Cl(3)	73	60	27	-4	26	3	87 (isotropic)					
P	27	32	22	1	6	1	35	27	64	5	-2	-2

B. Isotropic temperature factors.

	$\underset{\sim}{1}$	$\underset{\sim}{2}$		$\underset{\sim}{1}$	$\underset{\sim}{2}$
C(1)	41	30	C(21)	28	24
O	66	116	C(22)	35	39
C(2)	40		C(23)	43	62
C(3)	42		C(24)	45	55
C(4)	47		C(25)	43	56
C(5)	39		C(26)	42	45
C(6)	37		C(31)	33	43
C(7)	43		C(32)	44	54
C(8)	55		C(33)	56	73
C(9)		99	C(34)	51	57
Cl(4)		113	C(35)	52	74
Cl(5)		144	C(36)	45	67
C(11)	31	34	C(40)	32	61
C(12)	45	70	C(41)	32	42
C(13)	62	72	C(42)	36	60
C(14)	62	83	C(43)	52	80
C(15)	54	84	C(44)	65	71
C(16)	41	59	C(45)	57	63

TABLE A.3

Interatomic distances and angles in $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$ and $[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$

Distances and angles in the complex anions. The symbols X(1) and X(2) represent the mid points of the C(2)-C(3)and C(5)-C(6) bonds respectively. Primed atoms are related to unprimed by the symmetry operation (-x, y, ½-z).

	(1)*	(2)*
Ru - Cl(1)	2.422(2)	2.374(6)
Ru - Cl(2)	2.429(2)	2.418(6)
Ru - Cl(3)	2.445(2)	2.48(3)
Ru - C(1)	1.837(7)	1.88(5)
Ru - C(2)	2.197(7)	
Ru - C(3)	2.246(7)	
Ru - X(1)	2.111(7)	
Ru - C(5)	2.234(7)	
Ru - C(6)	2.206(7)	
Ru - X(2)	2.154(7)	
C(1) - O	1.161(10)	0.98(8)
Cl(1) - Ru - Cl(2)	97.44(7)	89.1(2)
Cl(1) - Ru - Cl(3)	87.18(7)	91.8(6)
Cl(1) - Ru - C(1)	83.4(2)	94 (2)
Cl(1) - Ru - X(1)	165.4(2)	
Cl(1) - Ru - X(2)	96.2(2)	
Cl(2) - Ru - Cl(3)	86.59(7)	86.7(6)
Cl(2) - Ru - C(1)	83.5(2)	176 (2)
Cl(2) - Ru - X(1)	96.6(2)	
Cl(2) - Ru - X(2)	166.0(2)	
Cl(3) - Ru - C(1)	165.3(2)	92 (2)
Cl(3) - Ru - X(1)	97.4(2)	
Cl(3) - Ru - X(2)	97.2(2)	
C(1) - Ru - X(1)	94.6(3)	
C(1) - Ru - X(2)	95.0(3)	
X(1) - Ru - X(2)	69.5(3)	

TABLE A.3 (contd.)

	(1) ~	(2) ~
Cl(1) - Ru - Cl(1)'		178.2(3)
Cl(1) - Ru - Cl(2)'		89.6(2)
Cl(2) - Ru - Cl(2)'		88.9(3)
Cl(3) - Ru - Cl(1)'		89.5(6)
Cl(3) - Ru - Cl(2)'		175.2(6)
C(1) - Ru - Cl(1)'		87 (2)
C(1) - Ru - Cl(2)'		92 (2)

TABLE A.3 (contd.)

Summary of subsidiary distances and angles. Mean σ values are based on the e.s.d.'s from least squares, σ (mean) values are from the spread of the n chemically equivalent values. Distances are given in Å and angles in degrees.

	n	min.	max.	mean	σ(mean)	mean σ
Cation in 1						
C - C	24	1.359	1.402	1.383	0.012	0.011
C - C	1	-	-	1.506	-	0.009
P - C	4	1.793	1.818	1.799	0.006	0.007
C - C - C	24	118.9	121.8	120.0	0.7	0.7
C - P - C	6	107.1	111.5	109.5	1.7	0.3
Cation in 2						
C - C	24	1.306	1.464	1.377	0.045	0.036
C - C	1	-	-	1.505	-	0.031
P - C	4	1.801	1.834	1.815	0.016	0.020
C - C - C	24	114.8	123.3	120.0	2.0	2.3
C - P - C	6	107.3	112.7	109.5	2.0	1.0
Norbornadiene in 1						
C - C	2	1.377	1.380	1.379	-	0.010
C - C	6	1.528	1.544	1.536	0.006	0.011
CH_2Cl_2 in 2						
C - Cl	2	1.747	1.767	1.757	-	0.032
Cl - C - Cl	1	-	-	108.3	-	1.7

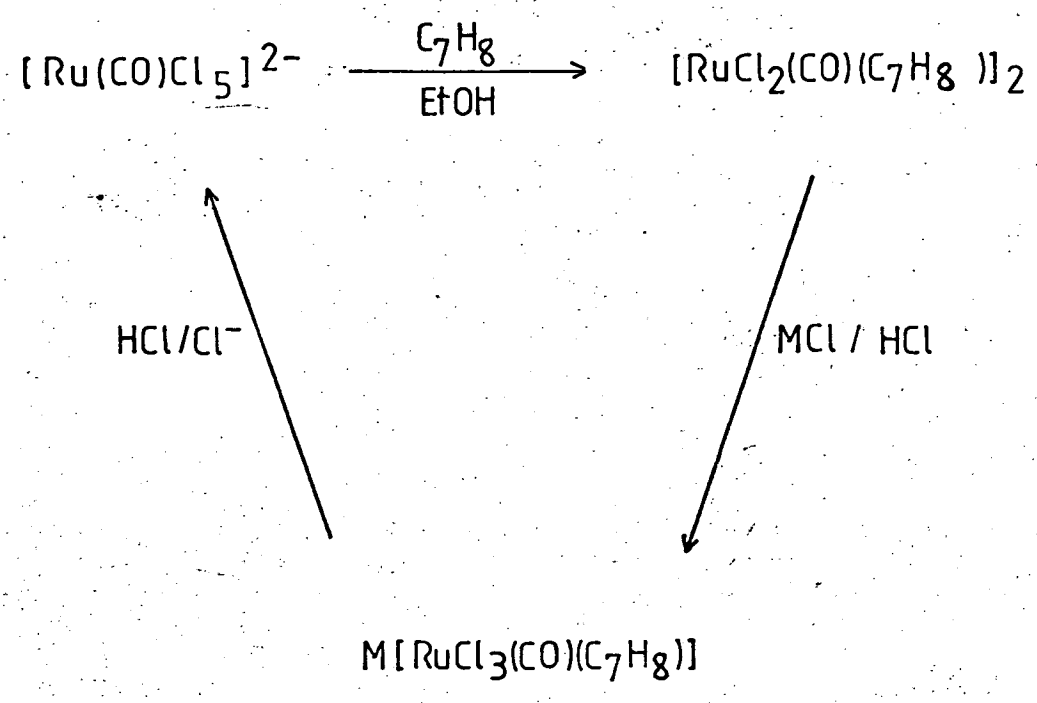
* (1) is $[PhCH_2PPh_3][RuCl_3(CO)(C_7H_8)]$

(2) is $[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$.

TABLE A.4

Carbonyl i.r. modes for various carbonylchlorometallate anions

Compound	$\nu_{(CO)}$ (cm^{-1})	Reference
$[NH_4]_2[RuCl_5(CO)]$	2059	133
$[PhCH_2PPh_3]_2[RuCl_5(CO)].2CH_2Cl_2$	1994	128
$Cs_2[RuCl_5(CO)]$	2015	135
	(2038	134)
$Cs_2[RuCl_4(CO)(H_2O)]$	1951	135
$Cs_2[RuCl_4(CO)_2]$	2035) 1945)	134
$Cs_2[RhCl_5(CO)]$	2117	135
$Cs_2[IrCl_5(CO)]$	2060	135
$Cs_3[OsCl_5(CO)]$	1968	135



SCHEME A.1 Formation of $[RuCl_3(CO)(C_7H_8)]^-$ and $[RuCl_5(CO)]^{2-}$

APPENDIX 2

Abbreviations used in the text

py	=	pyridine
en	=	ethylenediamine
bipy	=	2,2'-bipyridyl
phen	=	1,10-phenanthroline
mediphos	=	bisdiphenylphosphinomethane
etdiphos	=	bisdiphenylphosphinoethane
Ph	=	phenyl
C_7H_8	=	bicyclo[2.2.1]hepta-2,5-diene (norbornadiene)
C_8H_{12}	=	1,5-cyclooctadiene

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List of Postgraduate Courses Attended

Aspects of n.m.r. Spectroscopy by Dr. R.K. Harris

Double Resonance in n.m.r. Spectroscopy by Dr. W. McFarlane

Optical Properties of Transition Metal Complexes by Dr. T.A. Stephenson

X-ray and Neutron Elastic Scattering by Dr. R. Nelmes

E.R.C.C. Course on Programming in FORTRAN

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Departmental seminars and colloquia